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# CONTRIBUTIVE RESEARCH AND DEVELOPMENT

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Final Report for Period 22 December 1994 – 21 December 1999

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This technical report gives a summary of the research performed in the materials and physical sciences in support of the Air Force Research Laboratory's Materials Directorate under a Contributive Research and Development contract. The report contains an abstract covering the nature of the research and the results for each of the 209 tasks completed under the contract.

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## Preface

This Final Technical Report was developed under Air Force Contract F33615-94-C-5804, Contributive Research and Development. This contract was sponsored by the Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright Patterson Air Force Base, Ohio 45433-6533. The Materials and Manufacturing Directorate Project Manager was Mr. Philip Mykytiuk. The Systran Federal Corporation Project Manager was Dr. V. ("Nagu") Nagarajan.

# 1.0 OVERVIEW

This final report for Contract F33615-94-C-5804 describes the objectives and accomplishments of Systran Federal Corporation (SFC) from contract inception to the end of the technical effort on 15 December 1999.

During this period, SFC administered this Contributive R&D contract in response to the need to provide highly specialized scientists for short-term studies vital to the objectives of the Wright Laboratory.

## 1.1 Approach

Meeting the contractual requirements for this effort, Systran Federal Corporation (SFC) provided all technical and administrative management control over the project and the assigned researchers.

SFC identified and assigned a principal researcher(s) for each task requested by the Government. These researchers conducted investigations in the physical and engineering sciences and provided a level of effort in accordance with task assignments. The effort involved theoretical studies, analytical experiments, diagnostic and measurement techniques, and evaluation of systems, devices, and concepts. Areas of investigation included chemistry, physics, polymers, metallurgy, ceramics, nondestructive evaluation, and solid mechanics. A majority of the technical work was conducted at Wright-Patterson AFB in Laboratory facilities.

SFC exercised management control over all the administrative aspects of the contract including budgets, schedules, and project management reports. All support requirements including software, graphics, and documentation were provided by SFC's support staff. All reports were prepared in accordance with CDRL requirements.

## 2.0 ACCOMPLISHMENTS

A total of 209 tasks were defined during this contributive research and development program. Of this total, 199 tasks were completed, 10 were cancelled, and 0 were not issued.

For each technical task completed under this contract, a final report was submitted upon completion of the technical effort. Abstracts of these final reports are included in this document. Each abstract provides a summary of major activities for each completed task. No abstract has been prepared for either administrative or canceled tasks.

### 2.1 Documentation/Graphics

SFC completed all documentation and graphics requirements. Monthly R&D status reports were submitted for each task. In addition, performance and costs reports were submitted monthly for each task, accounting for current and cumulative manhours and funds expended per task. Manhour expenditure charts were prepared. Final technical reports were submitted for each completed task from the original input of each researcher. SFC has provided all graphics support for presentations and documentation.

### 2.2 Software

Software developed under any of the technical tasks was delivered at the completion of the task. Software was delivered on the media supporting the computer system within the Materials Directorate Branch for which the research was performed. User's manuals/instructions were developed and submitted to support this software, when required.

### 2.3 Equipment

All equipment and materials purchases to perform specific tasks during the project were transferred to the Government.

## 3.0 TASK ABSTRACTS

This section contains abstracts for all technical tasks completed under this contract. Abstracts appear in numerical order by Task Number.

TASK: 1

TASK TITLE: Project Management/Administration

TASK OBJECTIVE: To provide support activities necessary to establish project task orders and overall contract administration.

PROGRAM MANAGER: Milton E. Zellmer

DESCRIPTION OF WORK:

The contributive research and development project required extensive management and administration activities that were not readily charged to a specific task. These activities fell into three general categories:

1. Those contract management administrative requirements to establish planning and control procedures that applied to the project as a whole. Examples are status reporting, project management meetings, and other general overall project reporting.
2. Those management activities required to establish each of the task assignments. These activities could not be charged to the task since the task was not yet approved during this phase.
3. Recording and reporting the performance and cost for the overall management and administrative activities.

This task provided project management/administration from 22 December 1994 through 15 December 1995.

TASK: 2

TASK TITLE: Investigation of Advanced Metallic Composites

TASK OBJECTIVE: To develop an understanding of the relationships between the composition and microstructure of matrices, the bonding at fiber/matrix interfaces, and composite properties in advanced metallic composites.

SCIENTIST: Sunil G. Warrier, Ph.D.

DESCRIPTION OF WORK:

The objective of the research was to develop a fundamental understanding of the role of interface properties on the mechanical behavior of continuous fiber-reinforced titanium matrix composites. Specifically, the activities were aimed at determining the stress distribution in cruciform shaped specimens during transverse tension tests, identifying the failure mechanisms and quantifying interface properties during transverse tension, developing and characterizing alternate test procedures such as torsion testing in an effort to fail the interface from tangential shear stresses and examining the influence of interface properties on the fatigue crack growth behavior of composites.

In order to determine the stress distribution in cruciform shaped specimens during transverse tension tests, finite element was performed using the ANSYS code. Based on the finite element analysis, it was shown that the singularity at the free surface of the interface can affect the response of the composite during transverse testing. Stress analysis indicated that the cross-shaped specimen was successful in isolating the irregular state of stress present at the free surface from a debond event due to the applied stress. These results corroborated the experimental evidence that under the applied stress, debonding occurred in the interior of the sample. Furthermore, the ratios of the critical parameters in the specimen geometry were shown to be sufficient in producing uniform stresses in the direction of the applied stress over a large portion of the interface in the loading region before debonding initiated.

In a subsequent study, the micro-mechanical failure mechanism under transverse loading was examined using criteria based on both normal radial stresses and tangential shear stresses

supported by the interface. From finite element analysis of the stress distribution along the circumference of the interface and the experimentally determined onset of non-linearity in the stress-strain curve, a first estimate of the properties of the interface was proposed. Based on failure under the maximum radial stress criterion, the tensile bond strength of the interface was determined to be of the order of 115 MPa, whereas under the maximum shear stress criterion, the shear strength of the interface was about 180 MPa. The stress-strain curve generated from the finite element model using the interface bond strength of 115 MPa correlated well with experimental observations. Results of the finite element analysis also compared well with several simple analytical solutions. This study suggested that experimental observations of the onset of non-linearity in the stress-strain curve coupled with the finite element analysis of stresses in a single fiber cross-shaped specimen can be used to determine the effect of interface properties on composite behavior under transverse loading. However, since both normal radial stresses and tangential shear stresses co-existed due to the applied transverse tensile stresses, the study did not clearly identify the failure mechanism.

In order to clearly determine the failure mechanism, an alternate test procedure, torsion test, was developed. The objective of the torsion test was to fail the interface under the influence of only tangential shear stresses. This test was performed on several single SiC fiber reinforced Ti-6Al-4V composites of varying interfaces. Experimental results demonstrated the ability of the torsion test to cause interface failure by tangential shear stresses. An energy based fracture mechanics approach was used to draw a relationship between the applied torque, crack length and the frictional stresses. Based on this approach, a deviation from linearity in the measured strain as a function of the applied angle of twist was predicted when debonding occurred. From experimental observation of the onset of non-linearity in different composite systems, the interfacial tangential shear strengths of the SCS-6, AC1 and SCS-0 fiber-reinforced composites were estimated. Based on results and comparison with experimental observations and finite element analysis of transverse tension tests, the failure mode in SCS-6/Ti-6Al-4V and AC1/Ti-6Al-4V composite during transverse loading appear to be governed by the tangential shear failure of the interface.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 18, Stress Analysis and Failure Mechanisms During Transverse Loading of SiC/Ti-6Al-4V Composites.

TASK: 3

TASK TITLE: Alternative Bulk-Composite Material Shaft Design

TASK OBJECTIVE: To investigate the feasibility of integrating design and analysis technologies into a unified design system where material, process, and shape alternatives compete.

SCIENTIST: Adel Chemaly, M.S. and Bruce Webster, Ph.D., TechnoSoft, Inc.

DESCRIPTION OF WORK:

A package was developed to integrate the design and analysis of composite drive shafts. This package consists of external analysis codes and an AML model integrating these with the shaft geometry and knowledge model. An external stiffness code was developed specifically for this application; an external buckling code from another source was also used. The AML model contains the shaft geometry, knowledge of the shaft behavior, interfaces to the external codes, and a user interface. A specific shaft application case was analyzed for half meter long shaft with a design load of 2300 N-m. The laminate was constrained to have fibers in ±45° orientations. A final design consisting of 32 plies of graphite/epoxy (T300/5208) was determined to carry the stress and buckling loads. The outer diameter of the shaft was 3.8 cm. Additional analyses were performed to determine the performance of the shaft if allowed to operate under conditions of laminate damage. In this situation, the shaft design torque could be raised to over 5000 N-m indicating that either a smaller shaft or higher allowable load may be possible. This behavior may be limited by dynamic/fatigue considerations.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 24, Alternative Bulk-Composite Material Shaft Design.

TASK: 4

TASK TITLE: Application of the Rapid Foundry Tooling System (RFTS)

TASK OBJECTIVE: To evaluate cost effectiveness of using RFTS for variant sand casting.

SCIENTIST: Ron Cass, AI WARE, Inc. and Kim Schwartz, Columbiana Foundry Co.

DESCRIPTION OF WORK:

The Rapid Foundry Tooling System (RFTS) is a computer-based design tool for the rapid design of sand-casting patterns. Given the specification of a part in finished form, the Casting Module component of RFTS generates the geometry of a sand-casting pattern appropriate for fabricating the part. RFTS was created by AI WARE for the Kelly AFB foundry, however its usefulness is limited by its dependence on a particular solid modeling system. It is desired to evaluate the broader applicability of the system to commercial foundries, and to widen the capabilities of RFTS by allowing the rule-based components of the system to a wide range of commercial CAD systems.

This project was a commercialization effort composed of two parts. In the first, a non-trivial part design, provided by a commercial foundry, was transcribed in RFTS. The RFTS Casting Module functions were then used to generate models of a sand-casting pattern for the part, and a stereolithography model of those pattern pieces. In the second part of this effort, the design of the Casting Module of RFTS, which was originally integrated within a specific solid modeling package, was re-engineered in the form of a rigorous Functional Description/System Specification document.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 37, Commercialization of the Rapid Foundry Tooling System.

TASK: 5

TASK TITLE: Molecular Beam Epitaxy

TASK OBJECTIVE: Develop and apply techniques for molecular beam epitaxial (MBE) growth of strained layer superlattice materials.

SCIENTIST: J. Ken Patterson, Ph.D.

DESCRIPTION OF WORK:

The broad scope of this research task was to deposit and evaluate the electrical and crystalline qualities of thin film semiconductor materials that have relevance to technologies ranging from long wavelength Infra-Red (IR) detectors to high temperature electronics. Conventional elemental source Molecular Beam Epitaxy (MBE) was used for the growth of thin film crystals comprised of single layers and various layer sequences of InAs, GaSb, and AlSb compounds. Crystal growth conditions were monitored *in-situ* with Reflection High Energy Diffraction (RHEED), the analysis of which lead to the mapping of the kinetic (during film growth) surface reconstruction phase diagrams for InAs, GaSb, and AlSb. Several specific MBE layer structures were grown and analyzed with Double crystal X-ray Diffraction (DXRD) to determine the influence of growth conditions on layer interface roughness and state of strain relaxation, and Hall effect measurements for electrical transport properties such as free carrier concentrations and mobilities. Also, electron beam evaporation was used to sequentially deposit amorphous silicon (a-Si) and Ti thin film layers on SiC substrates; the thin film reactions caused by *in-vacuo* high temperature annealing of these structures were analyzed by thin film X-Ray Diffraction (XRD), Auger depth profiling, and *in-situ* sheet resistance measurements. Due to the potential application of the InAs,GaSb, and AlSb research to IR detectors, and the Ti/a-Si/SiC research to high temperature stable ohmic contacts, this research project was divided into two parts: IR detectors MBE work, and SiC contacts work, respectively.

**IR Detectors MBE Work:**

Due to their small band gaps, materials systems involving InAs and GaSb have been previously examined elsewhere on a theoretical level for application to long wavelength ($10<l<25$mm) IR detectors. The state of the art is that experimental results are needed to help ascertain whether the theoretical models being used are correct or not, as well as whether a GaSb/InAs based strained layer detector is feasible at all. This work placed a great deal of emphasis on determining the surface reconstruction phase diagrams for MBE growth of layers of GaSb, InAs, and AlSb in MLBM. Once this is known, all information concerning multiple film quality measurements may be clearly plotted on the surface phase diagram and then growth conditions that optimize any set of those film qualities may be unambiguously determined. Results

of this study include: Surface phase diagrams for MBE growth of InAs, GaSb, and AlSb; Interface roughness studies for InAs/GaSb layers indicating that GaAs like interfaces are significantly rougher than InSb like interfaces and; ¢Lift-off¢ results for separating InAs and GaSb films from their growth substrates show that the film crystal quality is not compromised as a result of the ¢lift-off¢ technique.

**SiC Contacts Work:**

Due to the relatively large bandgap of SiC (6H), ~3.0 eV, SiC is a reasonable candidate for high temperature electronic circuit applications. The constraint of high temperature stability of the circuits hinges on the ability to make high temperature stable contacts to the devices. This study selected a contact metallurgy ($TiSi_2$) that is well known in the silicon industry for its low resistance and stability, and examined the application to SiC (6H). Results include the determination of a minimum layer thickness of Si of 3000A for Ti thicknesses of 1000A which insures that the lowest resistivity and highest stability silicide $TiSi_2$ (C54) is formed. The minimum thickness of Si is required because it is found that significant amounts of carbon diffuse from the SiC substrate into the reacting silicide, and if the amount of C is enough (>10%) carbides form and tend to hinder the formation of the desirable (C54) polymorph of $TiSi_2$.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 33, Growth and Studies of Thin Film Semiconductor Heterostructures in the InAs, GaSb, AlSb System, and Investigations of $TiSi_2$ Contact Metallurgy to 6HSiC.

TASK: 6

TASK TITLE: Ceramer Technology

TASK OBJECTIVE: Synthesis of high performance polymers amenable to state-of-the-art sol-gel processing.

SCIENTIST: Narayanan Venkatasubramanian, Ph.D.

DESCRIPTION OF WORK:

The emphasis of this project was the synthesis of novel thermoplastic resins with sulfonic acid pendants which have potential utility as matrix resins and as transparent hosts for mono-dispersion of second order NLO chromophores via specific association between the sulfonic acid function of the matrix and the amine base function in the chromophore. In analogy to the previously explored ceramers based on rigid-rod and extended-rod organic polymers, the thermoplastic resins would also be amenable to sol-gel processing with silicon alkoxides containing amino functions. High molecular weight polyarylene ethers with sulfonic acid pendants, especially sulfo-polyarylene ether ketones have been synthesized and were found to be soluble in hydroxylic solvents such as alcohol and in polar aprotic solvents such as DMAc and NMP. The homopolymers form soluble trialkyl ammonium salts in alcohol but form insoluble suspensions when pyridine is employed as the organic base. Preliminary studies indicate that a second order NLO chromophore, 1-(4-pyridyl)-2-(2-thienyl)ethylene can be homogeneously dispersed in sulfonic acid-pendanted polyarylene ether ketones via formation of a pyridinium sulfonate.

A high molecular weight, 1:1 sulfonic acid-pendanted copolyarylene ether ketone was synthesized. This formed an insoluble suspension in alcohol but could not be solubilized in alcohol by trialkyl amines even after warming. Presumably, copolymers with higher sulfonic acid contents may be required for polymer solubilization via the formation of trialkylammonium salts.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 30, Syntheses, Properties, and Potential Applications of Sulfo-Pendanted Poly(Arylene Ethers).

TASK: 7

TASK TITLE: Modeling of Molecular Beam Epitaxy of Strained-Layer Heterostructures

TASK OBJECTIVE: Develop computer models for MBE growth of III-V heterostructures which describe alloy segregation and other physical phenomena observed during the growth of strained layers.

SCIENTIST: Krishnamurthy Mahalingam, Ph.D.

DESCRIPTION OF WORK:

Molecular beam epitaxy (MBE) of GaAs/$Al_xGa_{(1-x)}As$ heterostructures is often performed at substrate temperatures where considerable Ga desorption is observed. In-situ desorption mass spectroscopy studies have shown that the time evolution of the Ga desorption rate differs significantly during AlGaAs-on-GaAs interface formation and during growth of bulk AlGaAs, resulting in significant grading of the AlGaAs-on-GaAs interface.

In this study, a Monte Carlo simulation model was developed for MBE of GaAs/AlGaAs heterostructures wherein a configuration dependent Al-Ga exchange reaction and an attractive interaction between Al-Ga are included in order to explain the observed Ga desorption behavior. Simulations were performed for growth temperatures in the range of 970-1030 K, with flux conditions and growth rates the same as that reported in the experimental studies. The desorption rates of the individual species and the Al/Ga concentration profiles (during growth of AlGaAs) were obtained as a function of growth time.

The results from these simulations show that the transients in the Ga desorption rate during AlGaAs-on-GaAs heterointerface formation can be explained in terms of both, the surface exchange mechanism and attractive interaction between Al-Ga. However, only attractive interaction between Al-Ga can explain the reduction in Ga desorption rate during growth of bulk AlGaAs. A significant difference is observed in AlGaAs-on-GaAs interface stoichiometry predicted by models which either include only the exchange mechanism or attractive interaction between Al-Ga.

The effect of Al content on Ga behavior was also studied. The results from the model predict that increase in Al content reduces the Ga desorption rate, but has negligible effect on activation energy for Ga desorption.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 28, A Monte Carlo Study of Cation Desorption at Interfaces in III-V Heterostructures Grown by Molecular Beam Epitaxy.

TASK: 8

TASK TITLE: Metallurgical Phenomena in MMC Processing

TASK OBJECTIVE: To establish the importance of various metallurgical mechanisms in controlling consolidation and bonding during the fabrication of foil-fiber-foil, metal matrix composites (MMCs).

SCIENTIST: Perikles D. Nicolaou, Ph.D.

DESCRIPTION OF WORK:

This project contained two parts. The first part was the simulation of the hot tension test under cavitating conditions, while the second dealt with experimental physical modeling of the deformation of Ti-22Al-23Nb unreinforced consolidated foils.

A theoretical analysis of the isothermal hot tension test under cavitating conditions for sheet samples was performed using a ¢direct equilibrium¢ approach. The effects of cavity growth rate h, initial cavity volume fraction $C_{VO}$, strain rate sensitivity exponent m, strain hardening exponent n, and specimen taper on engineering stress-strain curves, strain profiles, and failure modes were established. During quasistable deformation, the required load for a cavitating material is slightly higher than that for a non-cavitating material because of strain rate and effective area effects. Model results also delineated the competition between failure controlled by localized necking versus fracture, the latter being defined by a critical volume fraction of cavities. Specifically, at low strain rate sensitivities m and cavity growth rates h, failure was predicted to be controlled by necking. By contrast, at high values of m and h, fracture prior to localized necking was predicted to predominate; in these cases, the cross-sectional area at the failure site was appreciable, thus resembling a form of brittle fracture.

In order to examine the effect of mechanical texture on the high temperature deformation of Ti-22Al-23Nb, unreinforced-consolidated-foil panels were fabricated. Material properties such as the flow stress, the strain rate sensitivity, the tensile elongation, and the anisotropy parameter were determined from tensile testing at 980°C and nominal strain rates ranging between $1.6 \times 10^{-2}$ to $1.6 \times 10^{-4}$ $s^{-1}$ for both the longitudinal and transverse direction. It was found that the flow

properties did not differ significantly between the two directions, although the tensile elongation was a little higher and the discovery parameter a little lower for the longitudinal as opposed to the transverse direction for all the testing conditions. The flow stresses between the longitudinal and the transverse direction were similar, except at the very low strain rates where deformation occurred under near superplastic conditions and grain boundary sliding was contributing to deformation.

The detailed report description, method, results and discussion are reported in Contributive Research and Development Final Report, Volume 19, A Theoretical and Experimental Investigation of the High Temperature Deformation of Monolithic Materials.

TASK: 9

TASK TITLE: Computational Chemistry Evaluation of Halon and Halon Replacements

TASK OBJECTIVE: To develop a fundamental understanding of the chemical mechanisms of Halon fire suppressant action through computational chemistry. To use this understanding to evaluate alternative compounds presently being considered, and other completely different compounds, for fire suppressant capability.

SCIENTIST: Rajiv J. Berry, Ph.D.

DESCRIPTION OF WORK:

*Ab initio* HF/6-31G(d) and MP2/6-31G(d) calculations were conducted to obtain the optimized geometries and vibrational frequencies for the reactants, transition state and products of the following two reactions of chlorofluoroethanes with the OH radical:

$CH_3$-$CF_2Cl$+OH®$CH_2$-$CF_2Cl$+$H_2O$
CHFCl-$CF_3$+OH®CFCl-$CF_3$+$H_2O$

High level *ab initio* G2-MP2 calculations were conducted at the MP2/6-31G(d) stationary point geometries in order to obtain reliable activation energies and reaction enthalpies for these reactions. The results of these calculations were used to carry out canonical transition state theory

calculations using zero-curvature tunneling correction (TST/ZCT) and hindered internal rotor approximations. Reaction rates were obtained over temperatures ranging from 200 K all the way up to temperatures likely to occur during combustion (~ 2500 K). Comparisons with experimental rates indicate that such a procedure can be used to obtain reliable rates over the available limited temperature range of the experiments (typically 200 to 900 K).

The potential energy of the transition state surfaces were scanned at the HF/6-31G(d) level in order to determine the barrier to internal rotation about the C-C bond (methyl rotor) and about the C...O (OH rotor). The C...H bond rotor was treated as a bend of the C...H...O angle, since this angle is nearly linear. The C-C internal rotation barrier for the two transition states was determined to be 15.1 kJ/mol (CF2Cl rotor) and 20.2 kJ/mol ($CF_3$ rotor). The OH rotation barriers were 5.4 and 4.1 kJ/mol, respectively. The calculated internal rotation barriers in conjunction with the experimental data can be used to compute rate expressions valid over a wide temperature range via the alternate less expensive conventional TST computation method.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume An Ab-Initio Investigation of the Thermochemistry and Kinetics of the Reaction of $CH_3$-$CF_2Cl$ and CHFCl-$CF_3$ with the OH Radical.

TASK: 10

TASK TITLE: Experimental Nondestructive Evaluation (NDE)

TASK OBJECTIVE: Analyze material response to ultrasonic excitation, develop theoretical models, and characterize advanced materials.

SCIENTIST: Peter B. Nagy, Ph.D.

DESCRIPTION OF WORK:

The main goal of this study was to investigate the feasibility of ultrasonic characterization of thin fibers from guided wave dispersion measurements. In order to establish a solid analytical background, first a unified general treatment of elastic guided wave propagation in anisotropic

multilayered fiber systems was developed. Dispersion relationships were derived from either free, immersed, or embedded fiber systems. Individual layers were assumed to be transversely isotropic with the axis of symmetry parallel to the axis of the fiber. Interface imperfections between any of the neighboring layers were accounted for by either the general transfer matrix of the interface zone or by a numerically tested on multilayered, microscopically anisotropic (textured) Silicon Carbide coated Carbon (SCS) fibers which are commonly used in state-of-the-art ceramic and metal matrix composites.

In the experimental part of this study we investigated whether the macroscopic anisotropy observed in coaxially layered SCS-6 composite fibers is entirely due to the structural anisotropy produce by the presence of microscopically isotropic and homogeneous constituents or, in addition, microscopic anisotropy caused by some texturing in the constituents themselves is also needed to properly model the fiber at ultrasonic frequencies. The dispersive behavior of the lowest order axisymmetric guided mode was used to assess the anisotropy of the fiber. Different ultrasonic velocity measurement techniques were tested to find the most suitable one for precision dispersion measurements. The best results were achieved by using a sharply focused immersion transducer to excite and detect the guided mode in the otherwise free fiber. The received dispersive signal was spectrum analyzed to obtain the frequency-dependence of the phase velocity. Very strong dispersion was found corresponding to more than 50% higher Poisson's ratio than the expected u » 0.18-0.2 value. A parametric study indicated that texturing in the silicon carbide cladding is the most probable cause of the observed anomalous phenomenon. Such texturing is expected from technological considerations, but to the best of our knowledge, has not been experimentally verified.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 20, Fiber Characterization from Ultrasonic Dispersion Measurements.

TASK: 11

TASK TITLE: Investigation of Advanced Metallic Composites

TASK OBJECTIVE: To develop an understanding of the relationships between the composition and microstructure of matrices, the bonding at fiber/matrix interfaces, and composite properties in advanced metallic composites.

SCIENTIST: Douglas B. Gundel, Ph.D.

DESCRIPTION OF WORK:

The ability of the fiber-matrix interface to support normal stresses is critical for transverse (90° to the fiber axis) strength and creep resistance of titanium-matrix composites (TMC's), which are proposed for use at elevated temperature in aircraft engines. Recently, a cruciform specimen geometry was developed to measure the remotely applied stress where interface debonding occurs in TMC's. Previously, the test has been used to measure debonding in single-fiber composites, but relatively few tests were performed and some appeared to have been influenced by poor consolidation of the composite.

In this project, a statistically significant number of single-fiber SCS-6 SiC fiber/Ti-6Al-4V specimens were tested, and those that contained poor consolidation were found and removed from the population. In addition, a range of specimen thickness was investigated, and this was found to have no influence on the remote debond stress. For single-fiber composites the average remote debond stress was found to be 322±14 MPa. Multiple-fiber specimens of single and four-ply configuration were also tested and the remote debond stress was found to be similar for these specimens, and the same as that determined from single-fiber specimens. The single-fiber test therefore gives important information regarding the load-carrying ability of the fiber matrix interface and, in the present case, can be used to directly predict the behavior of high volume fraction composites that are to be used in service.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 31, The Interface Debond Stress in Single and Multiple SiC Fiber/Ti-6Al-4V Composites Under Transverse Tension.

TASK: 12

TASK TITLE: Deformation Mechanisms in Gamma Titanium Aluminides

TASK OBJECTIVE To analyze, characterize, and understand the fundamental deformation behavior in gamma titanium aluminides.

SCIENTIST: Sriram Seshagiri, Ph.D.

DESCRIPTION OF WORK:

The research project was comprised of two parts. Part I dealt with microstructure characterization and deformation behavior of polysynthetically twinned (PST) g-TiAl crystals, and Part II dealt with the geometry and nature of pinning points of 1/2<110] unit dislocations in binary TiAl alloys. The goal of this research was to advance fundamental understanding of the deformation behavior of polysynthetically twinned (PST) gamma (g)-TiAl crystals. In order to do this, the as-grown microstructure needed to be fully characterized so that the subsequent deformation substructure could be interpreted in a more systematic fashion. The project thus focused on detailed results of the as-grown PST microstructure and limited deformation experimental results.

The starting material for the PST crystals was a cast ingot of nominal composition containing Ti-49at%Al, obtained by the plasma arc melting process from Duriron Company Inc. The cast ingot was subsequently HIP'ed at 1260°C under a pressure of 25 ksi for 4 hrs. Following HIP'ing, the ingots were X-rayed to check for soundness of the ingot. A portion of the material was subsequently homogenized at 1420°C (in the alpha-phase field) for ~20 mts. followed by water quenching. The homogenized alloy was then analyzed for its Al content in an scanning electron microprobe analyzer using a Ti-50 Al binary alloy as a standard. The chemistry of the alloy was also checked by X-ray fluorescence for Al and interstitial (O, C, and N) contents.

PST crystals from the ingot were grown in the form 0.5" (f) X~10" long rods. These rods were melted and resolidified using the induction float zone technique in a CRYSTALLOX, crystal growth facility. Samples in the edge-on orientation were metallographically prepared from each of the crystals for observation of the a2 lamellae under the SEM-BSEI mode. Statistical information pertaining to a2 and g lamellae thickness, spacing, periodicity, and volume fraction were generated from the crystals.

The microstructural parameters that control the deformation behavior of these crystals include the distribution of the thickness and spacing of both the a2 and g lamellae, and the volume fraction of the a2 phase. Results indicate that all the parameters vary interdependently with change in the crystal pull rates, with a strong inverse correlation between the mean a2 spacing and its volume fraction, for fixed Al content in the PST crystal. Correlation between the pull rates and parameters like the ration of the maximum: minimum thickness and spacing of both the lamellae are more complex. Further, for the first time it was shown that the spacing and thickness statistics follow a log-normal distribution in these materials. Compression test results show that the yield stress values are strongly dependent on the lamellae orientation to the stress axis, and the appearance of an increase in the yield stress at 800°C in the 0° oriented lamellae appears to be dependent on a2 volume fraction and hence on the nature of the distribution of the lamellae.

In the second part of this project, TiAl alloy buttons containing Al contents of 50 and 52 at.% were prepared by arc-melting high purity Ti electrolytic sponge and Al ingots. The cast buttons were heat treated as follows: 1300°C, 50 h®1150°C, 70 h®1050°C, 2 h®furnace cooled to 25°C. The average grain sizes produced were 300 and 500 mm in the 50 and 52 Al alloys, respectively.

Compression samples measuring 5mm x 5mm x 12.5mm were sectioned from the heat treated alloys and electropolished to remove surface damage. The samples were deformed to a plastic strain of ~1-1.5% at room temperature (RT), 300, 600, and 800°C under a constant strain rate of $1.7 \times 10^{-4}$ $s^{-1}$. Thin foils were sectioned from the deformed samples and prepared for TEM observations using standard twin-jet thinning techniques. Weak beam observations of the thin films were conducted using a double-tilt specimen holder in both, a Philips CM20 and JEOL 200FX electron microscopes, both operated at 200 kV.

The **b**=1/2<110] unit dislocations in binary TiAl alloys exhibit unique morphological characteristics which include (i) numerous pinning points along the screw segments, (ii) bowing out of the dislocation segment about these pinning points giving rise to a distinct cusped morphology, and (iii) the presence of dislocation debris in the form of prismatic loops or drawn out dipole segments in the vicinity of these pinning points. The results based on detailed weak beam stereomicroscopic observations show that the three dimensional arrangement of these dislocations is consistent with a *double cross-slip* process. It is argued that the morphological features, the

observed flow anomaly, and the experimentally measured activation volumes are all consistent with this process, and that jogs with varying heights created during the double cross-slip event act as strong obstacles to dislocation motion, and hence would have a significant contribution to the strengthening process.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 26, Deformation Behavior and Dislocation Mechanisms in TiAl Alloys.

TASK: 13

TASK TITLE: Develop and Implement Compatible Data Collection for Surface Analysis Equipment

TASK OBJECTIVE: To develop data collection and manipulation capabilities and implement them on existing surface analytical equipment.

SCIENTIST: Donald R. Thomas, M.S.

DESCRIPTION OF WORK:

The Surface Interactions Group of the Air Force Wright Laboratory's MLBM division operates a number of surface analysis systems. Each of these systems support one or more of the following analysis techniques:

- Auger electron spectroscopy (AES)
- X-ray photoelectron spectroscopy (XPS)
- Secondary-ion mass spectroscopy (SIMS)
- Ion-scattering spectroscopy (ISS)

This research project was an attempt to create a compatible data collection system that supports each of these techniques on each surface analysis system and will meet the following goals:

- Present a common interface across each of the surface analysis systems and across each of the analysis techniques.
- Create a modern, graphical-user interface, which is intuitive and easy to use.
- Allow exporting of data to a standard file format which can be imported into various third-party data processing software.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 21, Development of a Compatible Data Collection and Analysis System.

TASK: 14

TASK TITLE: Theoretical Characterization of Raman Spectra

TASK OBJECTIVE: To characterize the Raman spectra of b-aluminas for use in real-time control of chemical vapor deposition (CVD).

SCIENTIST: John F. Maguire, Ph.D., Southwest Research Institute

DESCRIPTION OF WORK:

There is an urgent need to develop improved *in situ* sensor technologies for on-line monitoring of the chemical state of polymeric and inorganic systems during materials and process operations. Often such applications require the analysis of matter in remote and hostile environments. In considering the many sensor technologies currently available, spectroscopic methods have clearly demonstrated considerable promise for remote, *in situ* applications both in terms of information content and the potential versatility and robustness of the instrumentation.

The modern adaptation of spectroscopy from an industrial view point takes advantage of the rapid advancements that have been made in a number of enabling technologies namely; fiber optics, intense monochromatic laser light sources, charged-coupled devices (CCD), and fixed dispersive elements. Techniques such as FT-Raman scattering; surface enhanced Raman spectroscopy (SERS); and coherent anti-Stokes Raman spectroscopy (CARS) show considerable promise in the industrial and environmental field, but are at least well developed, both theoretically and

empirically, for on-line sensor applications at the present time. Among this broad range of advanced spectroscopic techniques, fiber-optic FT-Raman scattering is the most applicable to the remote monitoring field because the small dimensions of the fiber allow it to be manipulated conveniently in practically any medium (e.g., solid, liquid, or gas); the fiber probe is tolerant of harsh environmental conditions; and the spectroscopic technique is capable of providing detailed information about the molecular state of the system.

While the instrumentation has improved significantly, there remain a number of technological areas in which further understanding of the fiber optic Raman technique is needed to fully realize its potential applications. For example, methods must be developed to allow better deconvolution of the observed spectrum. This, in turn, will require that the instrumental function can be better defined. The purpose of the work presented here was to examine the operational feasibility of the fiber optic Raman technique in one application of advanced materials processing: namely, the characterization of inorganic CVD coatings on high performance reinforcing fibers. Two important results were obtained in this initial investigation. Theoretical approaches were developed which allow interpretation of the spectra of these complex systems using methods which have a solid foundation in chemical physics. This is important for it means that this class of sensor will be useful in providing interpretable information in processing conditions which are atypical.

The ability of the fiber optic Raman method to obtain the vibrational spectrum of these complex inorganic systems provides an enabling and promising new industrial sensor technology for vacuum processes. The promise arises because not only can one detect spectra but also the information content of the spectra is amenable to a relatively straight forward interpretation. In the present work, molecular modeling methods were used to theoretically predict the Raman vibrational spectrum for simplified model systems. This provided the computational framework and tools needed to develop a tactic for assigning spectral peaks to the corresponding Raman-active vibrational modes of the model crystal structures.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 38, In-Situ Fiber Optic Raman-Rayleigh-Brillouin Spectroscopy (FORRBS) Sensor.

TASK: 15

TASK TITLE: Quantitative Fractography of Failed Components

TASK OBJECTIVE: To characterize, quantitatively analyze, and interpret the fractographic features on nickel base engine materials.

SCIENTIST: Nishkamraj U. Deshpande, Ph.D.

DESCRIPTION OF WORK:

In this study, quantitative microscopic and quantitative fractographic characterization of Air Force Aluminum-Lithium alloy AF/C-489 was carried out to understand the role played by microstructural parameters and fracture modes in controlling the fracture toughness of the alloy at ambient and liquid nitrogen temperature. It was found that both delaminations and extent of failure modes control the fracture toughness of the alloy. Further, increase in the extent of projected grain boundary area was seen to lead to reduction in fracture toughness.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 46, Quantitative Microscopic and Quantitative Fractographic Characterization of Aluminum-Lithium Alloy AF/C-489.

TASK: 16

TASK TITLE: Fracture Characterization of Ceramic Matrix Composites

TASK OBJECTIVE: To characterize the fracture characteristics of state-of-the-art ceramic composites under static and fatigue loading conditions for different crack geometries and orientations.

SCIENTIST: Jonathan J. Polaha, B.S.

DESCRIPTION OF WORK:

Ceramic matrix composites (CMCs) are becoming attractive candidates for high temperature structures because of their high strength and stiffness in such environments. However, interlaminar delaminations may exist in composite structures as a result of manufacture, assembly, or normal service usage. These delaminations may grow under normal loading conditions and may dramatically reduce the structure's strength, stiffness, and/or life. Therefore, delamination growth constitutes a critical failure mode which must be considered in the design of composite structures.

On this project, an approach was described for an investigation of the effect of mode ratio and elevated temperature on the fracture toughness of a unidirectional ceramic matrix composite. Different mode ratios were considered at both room and elevated temperature; pure mode I, pure mode II, and several mixed-mode conditions. The Double Cantilever Beam test and End-notched Flexure test were used to determine the critical strain energy release rates for mode I and mode II loading respectively. A relatively new test, the Single-Leg Bending test, was used to determine the critical strain energy release rate for the mixed-mode conditions. A compliance calibration technique was used for all three test methods. Fracture initiation loads were determined using a laser interferometric displacement gage to detect the corresponding onset of nonlinearity.

The detailed project description, method, results and discussion are reported in Contributive Research and Development Final Report, Volume 5, An Approach for Characterizing the Fracture Toughness of a Ceramic Matrix Composite as a Function of Mode Ratio.

TASK: 17

TASK TITLE: NDE and Aging Systems Technology Transition Development

TASK OBJECTIVE: Identify, analyze, and/or develop enhanced methods for technology transition of sonic, electromagnetic, radiographic, and optical methodologies for use in nondestructive evaluation (NDE) and in aging systems.

SCIENTIST: Matthew J. Golis, Ph.D., Advanced Quality Concepts

DESCRIPTION OF WORK:

This project provided assistance in the development of enhanced methods for technology transition of Nondestructive Evaluation (NDE) technologies between the private sector and the Wright Laboratory. A special emphasis was placed on matters relating to the aging systems within the U.S. Air Force. Project activities centered around three distinctly different types of tasks: (1) validation of inspection protocols using MLLP-developed ultrasonic transducers for inspection of aging C-141 aircraft for cracking in wet wing weep holes, (2) presentation of both weep-hole inspection results and applications of branch studies to private industry and branch personnel, (3) assisting in creating links between the branch's technical staff and private industry involved in aircraft component manufacture and repair.

The NDE technique validation task centered around conduct of field trials of the approach developed within the MLLP branch to inspect cracking weep holes in the lower wing planks of C-141 fuel tanks on behalf of the Warner Robins ALC (WR/ALC). The developed system was able to verify the presence of all the cracks found through eddy current techniques, and a measure of the signal response variations to be expected from naturally occurring cracks and from open holes with widely varying degrees of surface roughness both within the hole and on the outer surface of the wing skins.

Participation in several technology conferences took place in order to bring the activities of the NDE Branch to the attention of the private commercial sector. Sessions on NDE at the Spring conference of ASNT were chaired with papers given related to contracting activities and technical initiatives taking place at the NDE Branch. Another meeting attended on behalf of the NDE Branch was the annual Center for NDE gathering at Johns Hopkins University. The purpose of the meeting was to identify emerging NDE technologies which may have the potential for adaptation to areas of interest to the USAF.

The report recommends ways in which the Air Force NDE technologies can be transitioned to both the private sector and other agencies based on continued close interactions with key individuals active in the NDE field including manufacturers of aircraft components and systems.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 22, NDE and Aging Systems Technology Transition Development.

TASK: 18

TASK TITLE: Corrosion Prevention Technology for Paint for Life Coatings Systems

TASK OBJECTIVE: The Air Force requires development of Paint For Life Aircraft Coatings Systems which provide corrosion protection for aircraft surfaces throughout the life of aircraft. The objective of this task is to develop enabling corrosion prevention materials and processing technology for the new coatings systems. This corrosion prevention technology is based on a thorough, fundamental understanding of corrosion phenomenon as related to aircraft systems, and includes corrosion inhibitor mechanisms. The corrosion prevention technology will be incorporated into aircraft coatings systems beyond the year 2003.

SCIENTIST: Mohammad Khobaib, Ph.D., University of Dayton Research Institute

DESCRIPTION OF WORK:

This investigation was a part of a broader program which is directed towards the development of enabling corrosion prevention materials and processing technology. These advances will then be integrated in the "Paint for Life" coating system. The main objective of this study was to investigate and better understand the corrosion related problems faced during the development stage of the new coating systems. The study included the development of a thorough and fundamental understanding of the corrosion phenomenon as related to aircraft systems, including the mechanism of corrosion inhibition.

The first and foremost task was the establishment of a corrosion laboratory. At the same time, a literature survey was conducted to understand the corrosion prevention mechanism of surface treatments (conversion coatings) prior to the application of a primer. The review further supported the need for research in the area of single laser treatment and in the area of combined

laser and sol-gel treatment to obtain a corrosion resistant primer adherent surface. Simultaneously, a number of Al2024-T3 specimens were oxidized in laboratory air over an extended period of time and studies were conducted on the corrosion prevention behavior of the resulting oxide surface.

Finally, the corrosion prevention behavior of the coating system currently used by the U.S. Air Force was studied using a system-based approach, starting from the conversion coating to the complete system, which consists of the conversion coat, primer, and top coat.

The detailed project description, method, results & discussion are reported in Contributive Research & Development Final Report, Volume 39, Corrosion Prevention Technology for Paint for Life Coating Systems.

TASK: 19

TASK TITLE: Aromatic Polymers for Opto-Electronic Evaluation

TASK OBJECTIVE: The synthesis and characterization of unique aromatic polymers for evaluation as electronic conductors or nonlinear optical chromophores.

SCIENTIST: Girish S. Patil, Ph.D.

DESCRIPTION OF WORK:

The objective of the project was to synthesize polymers for opto-electronic applications. Target molecules chosen were novel aromatic heterocyclic polymers. During the course of this study some very interesting chemistry was encountered.

The study resulted in the successful isolation and full characterization of an unexpected product, xanthone 5, which was found during the attempted synthesis of bisbenzoxazole 4b. A plausible mechanism was put forth to account for its formation. It was also demonstrated that the formation of xanthone 5 can be avoided, and bisbenzoxazole 4b successfully synthesized, by changing the reaction conditions from strongly acidic to neutral.

The detailed project description, method, results, and discussion we reported in Contributive Research and Development, Volume 11, Novel Heterocyclic Polymers for Opto-Electronic and Structural Applications.

TASK: 20

TASK TITLE: Oxidation Effects in High Temperature Metals

TASK OBJECTIVE: The investigation and evaluation of oxidation effects on emerging high temperature metals.

SCIENTIST: George R. St. Pierre, Sc.D., Ohio State University

DESCRIPTION OF WORK:

The objective of this project was the evaluation of Wright Laboratory Materials Directorate research programs in the oxidation effects in high-temperature metals. Reviews of current programs were conducted with ML Work Unit Directive (WUD) leaders and ML Division Chiefs. New research initiatives were identified through interaction with the Air Force Office of Scientific Research (AFOSR), the Science Advisory Board, and the ML Executive Group.

Recommendations were made for development of plans for new high-temperature metals within ML programs, in close coordination with the ML Director.

The detailed project description, method, results, & discussion are reported in Contributive Research & Development Final Report, Volume 1, Oxidation Effects in High Temperature Metals.

TASK: 21

TASK TITLE: Investigation of Advanced Metallic Composites

TASK OBJECTIVE: To develop an understanding of the relationships between the composition and microstructure of matrices, the bonding at fiber/matrix interfaces, and composite properties in advanced metallics composites.

SCIENTIST: Awadh B. Pandey, Ph.D.

DESCRIPTION OF WORK:

This research was comprised of two parts. Part I dealt with "The Fracture Behavior of SiCp/Aluminum Alloy Composites with and without Large Aluminum Particles", and part II described "Processing and Fracture Behavior of SiCp/Al Alloy Composites". The main objective of this research work was to improve the fracture toughness of discontinuously-reinforced aluminum (DRA) composites. In part I, tensile and fracture toughness $J_{IC}$ measurements were performed on a powder-metallurgy processed SiCp/Al-7093 MMC with controlled heat treatments, and the damage mechanisms were evaluated to understand how microstructural parameters influence fracture toughness and crack resistance behavior. The modes and distribution of damage were also studied using tensile and fracture toughness tested specimens. In an effort to improve toughness, large Al particles were incorporated into the powder blend of MMC, and extruded to obtain pancake shaped Al-phases. These phases were rather inhomogeneously distributed in the composite. In the extruded condition, the effect of Al-particles on the initiation toughness was negligible. However, significant improvements were observed when the extruded material was further rolled for an additional reduction of approximately 70 percent. The specimen thickness and fatigue precracking had strong influence on the toughness of DRA. These issues were discussed in the context of observed deformation and damage mechanisms.

In part II, DRA composites were processed using a powder metallurgy route. A significant aspect of the approach was the successful use of blind-die extrusion for consolidation of powders, versus the more time-consuming vacuum hot pressing technique. The effects of particle size and alloy composition on tensile properties and damage modes were investigated, using 4.9 mm and 10.4 mm size SiC particles, and 2009 and 7091 aluminum alloys. The strength and ductility of the composites with the fine particles were higher than those with the coarse particles. The ductility of the SiCp/7091 composite was lower than the SiCp/2009 composite. In fine particle composites, damage was dominated by debonding, whereas in coarse particle composites, particle fracture was the dominant damage mode. This may explain the particle-size effect on composite ductility. Heat treatment did not influence the specific damage modes, but had a significant influence on damage localization in the gage section of tensile specimens.

The detailed project description, methods, results and discussion are reported in Contributive Research and Development Final Report, Volume 43, Processing and Fracture Behavior of Discontinuously Reinforced Aluminum Composites.

TASK: 22

TASK TITLE: Environmental Effects in Titanium Aluminides and Composites

TASK OBJECTIVE To characterize the mechanisms of environmentally induced damage accumulation in fatigue of gamma titanium aluminides and titanium matrix composites.

SCIENTIST: Andrew H. Rosenberger, Ph.D.

DESCRIPTION OF WORK:

The focus of this study was to conduct crack growth experiments in an ultra high vacuum (UHV) environment in order to detect environmentally-assisted crack growth phenomenon over the temperature range from ambient to 800°C. Scanning electron microscopy was used to examine the similarities and differences on the modes of crack advance as a function of environment. Effects of crack closure on the environmental difference in crack growth resistance were also examined.

Fatigue crack growth tests were conducted at the temperatures of 25°, 600°, and 800°C in laboratory air and UHV on; 1) TiAl forgings (designated ¢K5¢) with the nominal composition (in atomic %)Ti-47Al-3Nb-2Cr-0.2W having duplex and fine-grained lamellar microstructures, and 2) cast TiAl alloy having a nominal composition of Ti-47Al-1.5Cr-2Nb (designated 47-2-2).

Fatigue crack growth tests were conducted under load-shedding (decreasing K) and constant-load-amplitude (increasing K) using a computer controlled servohydraulic test machine. A high cyclic frequency, 10 or 20 Hz, was chosen to eliminate creep-fatigue interactions and promote an examination of the pure fatigue response to environment. A stress ratio ($R=s_{min}/s_{max}$) of 0.1 was used on all tests. Crack length and crack closure were determined using crack mouth opening displacement measurements on the compact tension specimens. High vacuum crack growth tests were conducted on a similar servohydraulic test machine fitted with a vacuum

chamber evacuated by a two stage turbomolecular pumping system. This chamber is capable of maintaining a vacuum of $3 \times 10^{-7}$ Pa with predominantly water vapor, nitrogen, and oxygen as the residual gasses with partial pressures of approximately $9 \times 10^{-8}$, $1 \times 10^{-8}$, and $3 \times 10^{-9}$ Pa, respectively. Elevated temperature tests were conducted using a tungsten mesh hot zone which had no appreciable influence on the vacuum level or residual impurities.

A pronounced environmental effect was observed under all temperatures examined with crack growth rates generally an order of magnitude lower in vacuum as compared to air. Subtle differences in crack growth mode were observed in some instances but were not necessary to cause the dramatic changes in fatigue crack growth resistance and increases in crack growth threshold.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 16, Environmental Effects in Titanium Aluminides and Titanium Alloys.

TASK: 23

TASK TITLE: Deposition and Characterization of Solid Lubricant and Hard Materials

TASK OBJECTIVE: To conduct research on the growth and characterization of solid lubricants and hard materials that provide low friction surfaces and/or wear protection. To design, assemble, and operate vacuum deposition equipment. To utilize a variety of standard analytical and tribological tests to determine mechanical and friction/wear properties of materials as part of the overall research and development program in advanced tribological materials.

SCIENTIST: Josekutty J. Nainaparampil, Ph.D.

DESCRIPTION OF WORK:

It was predicted by Liu and Cohen that Carbon Nitride in its beta form should have a hardness even greater than that of diamond. After this prediction numerous researchers used a variety of deposition techniques to make this material. The work in the last ten years reveals that energetic particle deposition is more successful than pyrolysis or shock wave compression.

In this work an energetic ion bombarded reactive sputtering in an electron cyclotron plasma was used to deposit carbon nitride thin films on steel substrates. C-Nx films were formed using a novel technique, biased target, in an Electron Cyclotron Resonance generated plasma. The film properties were measured using X-ray photon electron spectroscopy, scanning electron microscopy, and nanoindentation. The binding energy of carbon and nitrogen atoms in these films shows a characteristic shift pointing to a stronger bond between them. The average film hardness is not satisfactory. Film topography does not show any features but porosity of the coating is minimum.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 49, Deposition of C-Nx Thin Films in an Electron Cyclotron Resonance Plasma Using Biased Target Sputtering.

TASK: 24

TASK TITLE: Mechanical Behavior of Titanium Matrix Composites

TASK OBJECTIVE: To develop and optimize methods for characterizing the creep response and constitutive behavior of matrix materials used in titanium matrix composites (TMCs).

SCIENTIST: Sol R. Bodner, Ph.D. and Richard W. Neu, Ph.D.

DESCRIPTION OF WORK:

An effort has been underway to obtain the material constants of the titanium alloy, Timetal 21S, for use on the Bodner-Partom viscoplastic constitutive model. An initial set of constants was obtained by Neu (1993) based on data available at that time. With a more extensive data base and experience in applying the material model to actual problems, Zuiker and Sanders (Z-S) (1995) suggested a revised set of constants. The new set led to generally better agreement of the simulations with test data but the representations were not entirely satisfactory and some uncertainties in the procedure remained.

At 650°C, the reference material Timetal 21S indicates appreciable hardening during straining similar to that of pure copper at room temperature. To properly model such extensive relative hardening for copper, Bodner and Rubin (1994), Bodner and Lindenfeld (1995), and Bodner and Rajendran (1995) used a procedure to modify the hardening evolution equations by taking the hardening rate terms to be exponential functions of the state variables for hardening.

In the present exercise, the equations were modified to account for isotropic hardening which dominates the response characteristics with the revised constants of Z-S (1995). This procedure introduces two additional material constants but is necessary for proper representations under extensive hardening conditions. Another important property of Timetal 21S at 650°C is the strong effect of thermal recovery of hardening. Examination of the response characteristics indicates that the coefficients of the simple power law expressions for thermal recovery should not be constants but should depend on the hardening variables. Again, with modification of the equations, two more material constants had to be introduced to account for the detailed effects of thermal recovery within the limitations of a simple power law. With these modifications, a set of material constants for the B-P model for Timetal 21S at 650°C were obtained.

An additional exercise was conducted to obtain a set of material constants at 482°C using the same modifications and minimizing the number of temperature-dependent constants. As shown in this exercise, the modifications to the B-P equations may be beneficial in reducing the number of temperature-dependent constants which somewhat offsets the addition of the four constants.

As a final exercise to compare the behavior at 650°C and 482°C, the inelastic strain rate was shown as a function of the steady state stress.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 6, Determination of the Material Constants of Timetal 21S for a Constitutive Model.

TASK: 25

TASK TITLE: The Analysis of Fatigue Damage in Ceramic Matrix Composites

TASK OBJECTIVE: To identify and document the development of damage in ceramic matrix composite under conditions of thermal and mechanical fatigue.

SCIENTIST: Shin S. Lee, Ph.D.

DESCRIPTION OF WORK:

Damage development and failure process play an important role in understanding mechanical behavior and developing of advanced fiber reinforced ceramic matrix composites. In this project, damage and failure process of four advanced CMC systems, KAISER, LANXIDE, HITCO, and GEN-IV, were characterized and documented. According to the mechanical behavior and damage development measured and observed in these systems, it suggests that these CMCs can be separated into two groups: (1) non-brittle, and (2) brittle CMCs. The high temperature long-term performance of non-brittle CMCs, KAISER and LANXIDE is strongly influenced by the thermal stability of protecting fiber coating. Damage enhanced environmental degradation was observed in the non-brittle system. On the other hand, the high temperature performance of the brittle system is controlled by the fiber systems, especially, the GEN-IV (oxide/oxide) system. In addition, based on the fatigue and creep test results, life prediction models for these CMCs were developed to simulate the high temperature long-term performance of these CMCs.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 7, Progressional Damage and Life Prediction of Advanced High Temperature CMCs.

TASK: 26

TASK TITLE: Global Optimization and Dynamic Properties of the Ground and Excited States of Conjugated Polymers

TASK OBJECTIVE: To further understanding of the microscopic mechanisms involved in the conduction of charge in fully conjugated conducting polymers.

SCIENTIST: Xiaofeng Duan, Ph.D.

DESCRIPTION OF WORK:

Polarizabilities, first and second hyperpolarizabilities for four small carbon-sulfur species: $CS_2$, $CS_3H_2$, $[CS_3]^{2-}$ and $[CS_3H]^-$ were investigated with *ab initio* calculations at both self-consistent-field (SCF) and second-order many-body perturbation theory (MP2) levels of theory. The static properties were computed via a finite-field method from the perturbed energies of the molecule in the presence of a homogeneous electric field. Three basis sets DH*, DH* augmented with diffuse p and d functions (DH*+pd), and 6-311++G** were used to investigate the effects of basis sets on the calculated properties at both SCF and MP2 levels. The calculations indicate the MP2/DH*+pd gives the largest hyperpolarizabilities for all the systems, while calculations with either HF/DH* or MP2/DH* result in unreasonably small or even negative hyperpolarizabilities. Among the four diffuse systems, $[CS_3]^{2-}$ anion gives the largest g value. The frequency dependent polarizabilities were also studied with time-dependent coupled perturbed Hartree-Fock (TDHF) method with an external field frequency ranging from 0.00 to 0.05 a.u. The results are encouraging for further studies of the ionic compounds of the trithiocarbonate anion as third-order nonlinear optical chromophores.

The understanding of how the band-gap changes with the variation of polymer length is important for the understanding of the electronic properties of narrow-gap semi-conducting polymers. The electronic structures and band-gaps as modeled by the energy difference between ground singlet state and excited triplet state of a series of oligomers of a polymer based on squarelene and fused thiophenes were investigated. AM1 semi-empirical calculations, Hartree-Fock (HF) and second-order Meller-Plesset perturbation (MP2) ab initio calculations, numerical atomic orbital basis set density functional theory (DFT) calculations and ab initio calculations which are based on the planewave local (spin) density functional method were employed to conduct the research. All the results of the different theories demonstrate that a narrow gap of about 0.5 eV or less could be reached with infinite polymer length.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 34, Theoretical Studies: I. Non-Linear Optical Properties of Diffuse Chemical Systems; II. Electronic Structures and Band-Gaps of Conjugated Polymers.

TASK: 27

TASK TITLE: Gallium Arsenide - Indium Gallium Phosphide Superlattices

TASK OBJECTIVE: Evaluate quality of quantum wells and superlattices grown by molecular beam epitaxy composed of GaAs and GaInP. Determine the effect of growth conditions on the electrical and optical properties.

SCIENTIST: Mohamed Ahoujja, M.S., University of Cincinnati

DESCRIPTION OF WORK:

The primary objective of this research project was to investigate the physical properties of the GaSb/InAs/GaSb superlattices. These materials are of great technological importance because the band gap of GaSb/InAs can be tuned by adjusting the InAs well thickness. Thus it is possible that very efficient variable wavelength infrared detectors could be fabricated from such superlattices. Because of the GaSb/InAs type-II band alignment, for an InAs layer thickness greater than 1000A, the conduction band edge of InAs overlaps with the valence band edge of GaSb, resulting in an intrinsic transfer of electron from the GaSb layer to the InAs layer. But due to the presence of donor interface defects, the electron concentration is often larger than the hole concentration. Thus, the GaSb/InAs type II heterostructure is a system that is of great interest both to the material community as a possible prototypical system to probe directly interface effects, and to the technical community as a possible highly efficient infrared detector.

In this project, advanced techniques for investigating the electrical transport coefficients of semiconductors of multi-carrier nature were used. Both the conventional mixed conduction and the "mobility spectrum" models were used to analyze the magnetic field-dependent Hall measurements at different temperatures. Both the electron and hole concentrations were found to be high due to the fact that these concentrations are distributed through a 20 period superlattice. So to get the carrier concentration per well per period, all the concentrations must be divided by 20. It was also found that a hybrid approach of the two methods is very useful in that they are complementary.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 8, Magnetic Field-Dependent Hall Measurements on GaSb/InAs Superlattices.

TASK: 28

TASK TITLE: Shubnikov-de Haas Effect in Semiconductor Heterostructures

TASK OBJECTIVE: Evaluate the quality of semiconductor heterostructures made of III-V semiconductors containing antimony and determine the effect of intrinsic defects both in the bulk of the semiconductor layers and at the interfaces of different semiconductors on the carrier concentration in the superlattices.

SCIENTIST: Ikai Lo, Ph.D.

DESCRIPTION OF WORK:

The objective of this project was to search for new materials for the applications of infrared photoelectronic detectors and high speed devices. The work had two directions to investigate the electronic properties of AlInAs/GaInAs quantum wells. One was the persistent photoconductivity effect and the other was the effect of barrier material.

The persistent photoconductivity effect was studied in d-doped $Al_{0.48}In_{0.52}As/Ga_{0.47}In_{0.53}As$ heterostructure samples by Shubnikov-de Haas and quantum Hall effect measurements. The well defined two-subband occupied two-dimensional electron gas was detected. The persistent photoconductivity was produced by illuminating the samples at about 4.2K with a red light emitted diode for different time period. The electron densities of the first and second subbands for the sample with pre-annealed substrate were increased by the illumination from 17.3 to 18.2 x $10^{11}$ $cm^{-2}$ and 3.6 to 4.1 x $10^{11}$ $cm^{-2}$, respectively. The onset of the second subband occurs at $n_0$ = 10.3 x $10^{11}$ $cm^{-2}$. It was also found that the concentration of deep donor traps is about 1.4 x $10^{11}$ $cm^{-2}$ and the deep donor traps are not affected by the pre-annealed substrate. It is believed that the model to describe the PPC effect in semiconductor heterostructure samples needs to be extended to those deep donor levels below Fermi energy and it does not have to be the DX center.

In the band engineering for the semiconductor epilayers, the band offset of a quantum well can be changed by using different barrier alloy. By varying the alloy composition, the lattice constant can be adjusted to match the substrate or the strain in the epilayer, and finely adjust the band offset to meet one's needs. In this study, we investigated the two-dimensional electron gas in the d-doped AlAsSb/GaInAs and AlInAs/GaInAs quantum wells, which are lattice-matched to InP substrate.

Two oscillations were observed due to the first two subbands of 2DEG in d-doped $AlAs_{0.56}Sb_{0.44}/Ga_{0.47}In_{0.53}As$ and $Al_{0.48}In_{0.52}As/Ga_{0.47}In_{0.53}As$ quantum well. From the electron densities of the two subbands, the energy difference between the first two subbands, $DE_{01}$, was found to be 72 meV for the $AlAs_{0.56}Sb_{0.44}/Ga_{0.47}In_{0.53}AS$, and 54 meV for the $Al_{0.48}In_{0.52}As/Ga_{0.47}In_{0.53}As$ quantum well. By comparing with the data from an $Al_{0.24}Ga_{0.76}As/Ga_{0.78}In_{0.22}As$ quantum well, it was found that the larger band offset sample gives the higher $DE_{01}$, but when the band offset is relatively small, the well width may determine the energy difference $DE_{01}$.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 9, Shubnikov-De Haas Effect in Semiconductor Heterostructures.

TASK: 29

TASK TITLE: Lubrication Phenomena in Self-Lubricating Metal-Matrix Composites

TASK OBJECTIVE: Establish the lubrication phenomena in self-lubricating aluminum metal-matrix composites dispersed with transition metal dichalcogenides.

SCIENTIST: Somuri V. Prasad, Ph.D.

DESCRIPTION OF WORK:

This project dealt with the mechanisms of lubrication in self-lubricating aluminum metal-matrix composites (MMCs). The composite was comprised of 5 percent by volume of tungsten disulfide ($WS_2$) and 10 percent by volume of silicon carbide (SiC) dispersed in a commercial

aluminum alloy (Al-0.40Si-0.75Mg) matrix. Friction and wear tests were performed on polished MMC surfaces using a 440C steel ball. The test environment was laboratory air with 55-65% RH; the tests were run for a duration of two million cycles. The wear debris was characterized by transmission electron microscopy (TEM). TEM samples were prepared by ultramicrotomy. Wear scars and transfer films on steel balls were analyzed by scanning auger microscopy and electron probe microanalysis.

Tungsten disulfide platelets were not detected either in the wear debris or in the wear transfer films on the steel counterface. The debris was predominantly spheroidal in shape. The debris and the transfer film were different in chemical composition from any of the constituent phases of the MMC. Transmission electron microscopy analysis of the debris confirmed the formation of new phases as a result of tribochemical reactions: $WO_3$, AlO(OH), and several unidentified phases. The largest volume fraction of the debris was found to be an amorphous, sponge-like material. Sliding of tungsten disulfide platelets does not appear to be a probable mechanism of lubrication. A new mechanism based on the formation of a sulfur based liquid phase comprised of sulfur with minute quantities of iron was proposed to explain the lubricating behavior of Al-SiC-$WS_2$ metal-matrix composites. The synergistic role played by porosity, SiC and $WS_2$ in imparting self-lubrication to the aluminum MMC was examined.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 14, Mechanisms of Lubrication in Self-Lubricating Aluminum Metal-Matrix Composites.

TASK: 30

TASK TITLE: Evaluation of Ceramic Composites for Turbine Engines

TASK OBJECTIVE: Characterize and evaluate four composite systems for use in augmenter nozzles of Air Force turbine engines and provide constructive feedback to the manufacturers.

SCIENTIST: James M. Staehler, M.S.

DESCRIPTION OF WORK:

This work was related to the ARPA funded ceramic flap and seal insertion program. Three principle topics were addressed; fiber-matrix interface properties, evaluation of engine tested secondary divergent flaps, and material characterization. Within these topics were a number of sub-topics which focused more specifically upon certain key issues.

Relative to fiber-matrix interface properties there were three principle objectives: (i) to determine if prior mechanical loading had a significant effect upon the interface properties compared to the as received, (ii) to determine if moisture had a detrimental influence upon the interface properties of a BN fiber coated composite compared with the as received, (iii) to determine if there was an intermediate or pest temperature problem related to the interface in a BN fiber coated composite. Each of these objectives was approached using fiber push-in techniques to measure interfacial properties. No attempt was made to correlate any of these influences with other aspects of the composites such as fiber degradation or matrix degradation. The effort focused upon two ceramic matrix composites; Nicalon$^{TM}$/BN/SiC/$Al_2O_3$ and Nicalon$^{TM}$/BN/SiNC. Primary results indicated that room temperature tension-tension fatigue testing of the former material at 150 MPa for $10^6$ cycles had no appreciable effect upon the mean interfacial properties. Elevated temperature (1000°C and 1100°C) tension-tension fatigue and creep rupture had some effect upon the mean interfacial properties of the later material. However, the pest temperature issue did not appear to be strongly rooted in a fiber-matrix interface effect. Some of the intermediate temperature work must be continued. Moisture exposure of the Nicalon/BN/SiNC material (90% relative humidity at 32.2°C) for two weeks did not appear to have an appreciable effect upon the mean values of the interfacial properties either. However, as in a lot of the other interfacial studies, the exposure actually seemed to reduce the scatter in the data.

For the evaluation of the engine tested flaps, much of the work is waiting upon completion of the engine testing. As a result, no data was available. However, Nextel610$^{TM}$/AS and Nextel720$^{TM}$/AS composite panels were evaluated in the lab under thermal cycle conditions. The Nextel 610 panel failed and the Nextel 720 panel survived 266 thermal cycles.

Other issues included the measurement of fiber volume fractions, densities, and specific surface areas in several different lots of an oxide-oxide CMC. The strengths of these CMC's

appeared to vary from lot to lot. The objective was to see if this could be correlated with some structural features.

The detailed project description, method, results, and discussion are reported in Contributive Research Development, Volume 13, Fiber-Matrix Interfacial Studies in Two BN Fiber Coated Systems.

TASK: 31

TASK TITLE: Processing and Characterization of Large Test Specimens of Graphitic Microcellular Foams from Anisotropic Pitch.

TASK OBJECTIVE: To process large specimens of graphitic microcellular foams and evaluate the mechanical and microstructural characteristics.

SCIENTIST: Debashis Dutta, Ph.D., Wright Materials Research

DESCRIPTION OF WORK:

This project dealt with the processing and characterization of microcellular foams from mesophase pitch. It has been hypothesized that reticulated graphitic foams, with strut sizes of the order of carbon fibers, will have excellent mechanical properties. It was demonstrated in the previous efforts that such graphitic microcellular foams can be successfully processed by the homogeneous nucleation technique. The foams were generally open celled, with strut sizes of the order of carbon fibers. Polarized light microscopy showed alignment of the graphene planes along the strut axis. But, the drawback was that the sample sizes were not large enough to do the relevant mechanical tests. To overcome this problem, a 1.6 gallon pressure vessel was modified so that larger samples could be processed.

Systematic studies were done to evaluate the effect of sample thickness, processing temperature, and saturation pressure on the foam morphology and properties. From these experiments, we were able to identify the processing window that produced foams with the desirable morphological characteristics, and improved mechanical properties. Using these results,

we started processing larger quantities of foams, so as to do a thorough mechanical and other property evaluation.

The detailed project description, methods results, and discussion are reported in Contributive Research and Development, Volume 4, Processing and Characterization of Graphitic Microcellular Foams from Mesophase Pitch.

TASK: 32

TASK TITLE: Carbon Composites Processing

TASK OBJECTIVE: To provide advanced innovative concepts, which will enable the synthesis and processing of lightweight, composite structural and thermal management materials for dual-use applications in air and space weapon systems and commercial products, particularly as enabling materials for thermal energy conversion processes.

SCIENTIST: Joseph W. Hager, Ph.D.

DESCRIPTION OF WORK:

There was no final report received for this task.

TASK: 33

TASK TITLE: Mechanisms of Fatigue Damage in Titanium Composites and Intermetallics

TASK OBJECTIVE: To study the mechanisms of fatigue damage in titanium alloy composites and intermetallics, and develop physically based models of the damage process.

SCIENTIST: J. Wayne Jones, Ph.D.

DESCRIPTION OF WORK:

Fatigue crack growth studies were conducted on a two-phase alloy with a nominal composition of Ti-46.5Al-3Nb-2Cr-0.2W (at %), heat treated to produce duplex and lamellar microstructures. Fatigue crack growth tests were conducted at 23°C using computer controlled servohydraulic loading at a cyclic frequency of 20 Hz. Several methods were used to obtain fatigue crack growth rate data, including decreasing-load-range-threshold, constant-load-range, and constant-$K_{max}$ increasing-load-ratio crack growth control.

The lamellar microstructure showed substantial improvement in crack growth resistance and an increase in the threshold stress intensity factor range, $\Delta K_{th}$, when compared with the behavior of the duplex microstructure. Stress ratio had a significant influence on crack growth behavior in both microstructure, compared to the duplex microstructure. In addition, limited shear ligament bridging and secondary cracking parallel to the lamellar interfaces were observed in the fully lamellar microstructure during fatigue crack propagation. These observations were incorporated into a model which analyzes the contribution of intrinsic versus extrinsic mechanisms, such as shear ligament bridging and roughness induced crack closure, to the increased fatigue crack growth resistance observed for the fully lamellar microstructure.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 74, Mechanisms of Ambient Temperature Fatigue Crack Growth in Ti-46.5Al-3Nb-2Cr-0.2W.

TASK: 34

TASK TITLE: Multiaxial Deformation of Titanium and Titanium Aluminide Alloys

TASK OBJECTIVE: To establish the effects of concurrent, multiaxial deformation on breakdown of lamellar microstructures in titanium and titanium aluminide alloys.

SCIENTIST: K.H.G. Ashbee, Ph.D.

DESCRIPTION OF WORK:

In the course of carrying out hot bidimensional compression tests, and sequences of differently oriented hot single upset forgings, on titanium and titanium aluminide alloys, microstructural studies have confirmed the overriding importance of plastic shear as the physical mechanism whereby large deformations are achieved during hot working processes.

The purpose of the experiments performed on this project was to compare the cumulative effect on microstructure of equal true strains applied parallel to a co-ordinate system of axes, a thermomechanical process that has been dubbed "abc" forging, with that of a true strain, of magnitude matching the cumulative strain in "abc" forging, but applied in a single upset, i.e. by conventional forging. Two as-cast alloys were selected for this study, namely Ti - 6 at% Al - 4 at% V and Ti - 44.7 at% Al -2.0 at% Nb - 2.0 at% Cr.

Both of the alloys studied are phase mixtures, so the compatibility of unequal finite strains during large overall deformations was a major theme underlying the experimental and theoretical work. Both alloys were observed to undergo large-scale coarsening of grain size during hot bidimensional compression, suggesting that this may be a convenient strain anneal method for growth of single crystals. The work culminated in the discovery that remarkably large torsional creep - shear strains in excess of 10%, and shear strain rates faster than $10^{-2}$ $s^{-1}$ - occurs in titanium aluminide phase mixtures subjected to pure shear stresses of the order of 100 MN $m^{-2}$ at temperatures near 1,000K.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 42, Multiaxial Deformation of Titanium and Titanium Alloys.

TASK: 35

TASK TITLE: Study of the Nonlinear Optical Properties and Charge Carrying Quasi-Particles in Electroactive Organic Polymers

TASK OBJECTIVE: (1) A determination of the two-photon cross section of selected nonlinear optical materials. (2) A description of the mobility and time-dependent properties of the charge carrying quasiparticles in electronically conducting polymers.

SCIENTIST: Guru P. Das, Ph.D.

DESCRIPTION OF WORK:

With a view to elucidate and develop a model for the mechanism of conduction in doped transpolyacetylene, an *ab initio* study was made of the ground and excited state of transoctatetraene in the presence of an Iodine atom. While the ground state was calculated as characterized by a slightly distorted alternating bond geometry with Iodine remaining largely neutral atop the plane of the polyene near roughly the midpoint of chain axis, the excited state has the geometry characterized by a solitonic distortion with the octatetraene carrying a net positive charge close to .7e. The bandgap (the gap between the highest occupied molecular orbital (HOMO) energy and the lowest unoccupied molecular orbital (LUMO) energy) was computed to be nearly .8 eV. Moreover, the excited state energy appears very insensitive to the position of Iodine along the axis of the octatetraene chain. As an extension of an earlier calculation on the transport of charge by a charged soliton, a similar calculation was performed on a $C_8H_{10}^+$ "kink" traveling along the backbone of $C_{12}H_{14}^+$ yielding very similar results.

A computer code was developed to compute the transport velocity of charge based on the above model and can be used in conjunction with the GAMESS program package.

A model for calculating two-photon absorption (TPA) intensities in conjugated systems was presented. The semiempirical package MOPAC was used to generate energies and transition moments via a configuration interaction (CI) involving single and double excitations. The evaluation of TPA cross sections were carried out by the sum-over-states (SOS) approach. The linewidth parameters associated with the inhomogeneous broadening effects were estimated from the one-photon absorption cross section data. The model was then illustrated by applications to some organic systems.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume Study of Charge Transfer in Conducting Doped Polyenes and Two-Photon Absorption in Non-Linear Optical Materials.

TASK: 36

TASK TITLE: Development of a New Approach to Fracture Mechanics

TASK OBJECTIVE: To develop improved models for fracture mechanics analysis of crack tips to enhance current capabilities for life prediction involving fatigue crack initiation and growth.

SCIENTIST: Glenn B. Sinclair, Ph.D. and Gautam Meda, Ph.D., Carnegie Mellon University

DESCRIPTION OF WORK:

The stress fields in angular elastic plates in extension were first treated by M. Knein and subsequently systematically identified by M.L. Williams. These studies revealed the possibility of elastic stress singularities at the vertex of the wedge. Such fields are at variance with the assumptions underlying the theory from which they came. Consequently, care needs to be exercised in interpreting them. Even with care, resulting inferences with respect to structural integrity are not always as reliable as desired in practice. Accordingly it is of some interest to explore alternative models which are free of these nonphysical singular stresses. This project considered a means to this end, namely the introduction of cohesive stress-separation laws.

The nature of the stress field occurring at the vertex of an angular elastic plate in extension was reconsidered. An additional boundary condition was introduced. This boundary condition reflects the action of cohesive stress-separation laws. Companion asymptotic analysis proceeded routinely on employing coupled eigenfunction expansions. Results show that a number of configurations that had previously been plagued with stress singularities become singularity free.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development, Volume 17, The Influence of Cohesive Stress-Separation Laws on Elastic Stress Singularities.

TASK: 37

TASK TITLE: Computational Modeling in Intermetallic Alloys

TASK OBJECTIVE: To apply computational techniques toward the exploration of fundamental behavior of intermetallic alloys, as well as to explore methods by which microstructural evolution may be modeled.

SCIENTIST: J.P. Simmons, Ph.D.

DESCRIPTION OF WORK:

Flow stress behavior in g-TiAl has two unusual aspects: (1) a steep drop in flow stress with increasing temperatures from 0 K and (2) an anomalous rise in flow stress as the temperature increases above 600-700 K. It has been suggested that these effects are caused by kink behavior. In this study, the properties of kinks on 1/2<110> dislocations in g-TiAl were simulated using Embedded Atom Method potentials. The specific geometry investigated was that in which the dislocation line was shifted by 1/4[112]. It was found that the core of this dislocation was diffuse, approximately 2 nm in length. The friction stress was found to be below $0.5 \times 10^{-3}$m. This result is consistent with the steep drop in flow stress at low temperatures, but casts doubt on the assertion that the anomalous flow stress is caused by kink configurations, since they do not provide substantial pinning force. It is suggested that the anomalous flow stress may be explained with a kink mechanism only if there is significant interaction of kinks with either solute atoms or kinks gliding on the cross-slip plane.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 29, Computational Modeling of Dislocation Kinks in Intermetallic Alloys.

TASK: 38

TASK TITLE: Advanced Stress Analysis for Composite Joints

TASK OBJECTIVE: To develop advanced stress analysis methods in support of ongoing projects on bolted and adhesive bonded monolithic and sandwich composite structures.

SCIENTIST: James M. Whitney, Ph.D.

DESCRIPTION OF WORK:

This project addressed the issue of free-edge stresses with emphasis on sandwich structure and bonded joints. The work was divided into three distinct parts.

In the first part an approximate technique was presented for obtaining free edge stresses in a sandwich beam. In particular, an analysis was presented within the framework of classical sandwich theory in which the face sheets are treated as laminates. In such a model free-edge boundary stresses cannot be satisfied. The original stresses were modified in the free-edge zone by adding functions which utilize the eigenvalue obtained from a model in which the sandwich beam was treated as a plate with a large length to thickness ratio. Coefficients to the added functions were determined such that free-edge boundary conditions were satisfied ply-by-ply. Interlaminar stresses at any point in the laminate were then obtained by integrating the equations of equilibrium from classical theory of elasticity. This resulted in the presence of interlaminar bending stresses in the face sheets as well as the core even though such stresses were neglected in formulating the macroscopic sandwich plate/beam equations. This modified stress approach provides a simplified method for determining free-edge stresses in sandwich beams.

In the second part the minimum number of kinematic variables in conjunction with higher order plate theories for approximating the stresses in the free-edge zone of a laminate under uniaxial inplane tension was examined. It is well recognized that classical shear deformation theory is not appropriate for such problems. The through-the-thickness normal strain component must be non-zero in order to obtain reasonable results. Two higher order theories were compared for approximating interlaminar stress distributions in the free-edge zone. These theories employ kinematic relations which lead to constant and linear distributions of transverse normal strain through-the-thickness of the laminate. Interlaminar stresses in the free-edge zone at the midplane and at the 0°/90° interface of a bidirectional laminate were considered. Difficulties associated with a constant through-the-thickness strain type theory in determining stresses at interlaminar locations

other than the midplane were also addressed. Numerical results indicate that stresses obtained from the linear through-the-thickness model are more accurate than those obtained from the constant strain model.

In the third part two problems associated with composite adhesive bonded joints were considered. In both cases free-edge stresses in conjunction with a higher order plate theory which includes linear through-the-thickness strain were the focus. In the first problem rail shear type of loading was applied, i.e. shear stresses were applied along the top and bottom surfaces with stress free boundaries along the two adjacent edges. Numerical results showed the higher order laminated plate theory is capable of producing both shear and normal stress distributions along the top and bottom surface which are consistent with classical theory of elasticity. The higher order plate theory provides a simplified approach compared to classical theory of elasticity. The second analysis was concerned with determining distributions of interlaminar shear and normal stresses at the centerline between notches in a double notch shear (DNS) specimen. Results showed that the interlaminar stresses are relegated to a very small zone near the notch tip with uniform axial stress developing a short distance outside this zone. Since the interlaminar stresses are produced in a very concentrated region with high stress gradients, the use of this specimen for measuring interlaminar shear strength is questionable. Solutions generated in conjunction with the DNS test illustrate that the higher order laminated plate theory provides a unified approach to the solution of free-edge problems associated with bonded joints.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 2, Advanced Stress Analysis for Composite Joints.

TASK: 39

TASK TITLE: Density Functional Modeling of Charged Quasi-Particles and Nonlinear Optical Properties of Electroactive Materials

TASK OBJECTIVE: Determine the feasibility of using the density functional formalism to model the structure and the static and dynamical properties of materials with strong electroactive characteristics.

SCIENTIST: Ryoichi Kawai, Ph.D.

DESCRIPTION OF WORK:

The objective of this project was to develop a method of "first principles" simulation that will describe the motion of large numbers of strongly interacting atoms (N » 500) with sufficient accuracy that reliable predictions of the properties of real systems of general composition may be made.

The ab initio molecular dynamics (AIMD) simulation code based on planewave-local density functional method was successfully implemented for a large unit cell polymer calculation using high performance fortran. The new code was installed on a new Silicon Graphics Indigo and massively parallel computer, Connection Machine model 5. The code is efficient enough to calculate electronic, geometric, and dynamical properties of large molecules and polymers. Various benchmark tests demonstrate the high degree of accuracy and efficiency of parallel processing. This code was applied to the simulation of polyacetylene and other large molecules.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 10, Development of Massively Parallel Ab Initio Molecular Dynamics Simulation Code for the Study of Large Polymer Systems.

TASK: 40

TASK TITLE: Modeling of Roughness Induced Crack Closure in Ti Alloys

TASK OBJECTIVE: To characterize the nature of fatigue crack fracture surfaces for use in developing analytical models of roughness induced crack closure in titanium alloys and intermetallics.

SCIENTIST: Ana M. Garcia

DESCRIPTION OF WORK:

A model for predicting and quantifying roughness induced crack closure was developed. By implementing a statistical approach to characterize contact between crack surfaces and using experimental data obtained using a laser scan microscope, closure levels for two Ti-Alloys were calculated. The results correlated with experimentally observed trends and showed that closure levels are highly sensitive to topographical parameters such as r.m.s of asperity heights, density of asperities, and radii of asperity tips. Furthermore, it was concluded that microstructural features such as lamellae vs. fine grain directly affect crack propagation.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 3, Modeling Roughness Induced Crack Closure in Ti-Alloys.

TASK: 41

TASK TITLE: Threshold Crack Growth Behavior in Titanium Alloys

TASK OBJECTIVE: To evaluate the near-threshold crack growth behavior in titanium alloys under high cycle fatigue and combined high cycle/low cycle fatigue.

SCIENTIST: Yuri N. Lenets, Ph.D.

DESCRIPTION OF WORK:

Threshold conditions and near-threshold crack propagation behavior were experimentally evaluated in titanium alloy IMI 834 subjected to high cycle fatigue loading (load frequency 50 Hz), sustained loading and combined sustained/cycling (ripples with DK = 1 MPaÖm < $DK_{th}$) loading conditions. Crack growth tests on compact tension specimens of 5 mm thickness were conducted in laboratory air using a 25 kN MTS servo-hydraulic test machine. The direct current electric potential drop method was employed for instantaneous crack length measurements. At $K_{max}$ = 10 MPaÖm, fatigue crack growth threshold of the alloy tested in laboratory air according to the "jump-in" test method (i.e., in the presence of large cyclic plastic zone corresponding to R = 0.1) was found to be 2.8...3.2 MPaÖm. The results suggest that the presence of an intermittent loading block during which the crack remains dormant can affect a fatigue crack growth threshold value as well

as post-threshold crack propagation behavior. Under stepwise load increase, neither sustained nor ripple load was found to cause crack propagation in the tested material at K ($K_{max}$) <28 MPaÖm. The ripple-load cracking behavior of the material tested at $K_{max}$ ³ 28 MPaÖm in accordance with stepwise load increase technique could not be rationalized on a basis of low-temperature creep phenomenon and did not seem to be governed by maximum stress intensity. Accounting for possible practical significance of the ripple-load cracking phenomenon in the material tested, further research employing alternative experimental approaches are required to provide better understanding of the behavior.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 44, Threshold Crack Growth Behavior in Titanium Alloys.

TASK: 42

TASK TITLE: Corrosion Inhibition Using Organic and/or Inorganic Compounds

TASK OBJECTIVE: To study compounds for corrosion control to replace currently used AF products.

SCIENTIST: Joseph Zahavi, D.Sc.

DESCRIPTION OF WORK:

The major goals of this work were to conduct and to explore a technological survey on coating systems: their formation, degradation, and stabilization.

The basic structure of coating systems that are of interest to the Air Force aircraft consist of polymer primer coating on aluminum alloy substrate and a top coat polymer on the primer layer. The basic requirements of these coating systems are: (a) extended-life coatings and (b) chromate-free coating inhibitor. In view of the fact that chromates cannot be used anymore following the Environmental Protection Agency (EPA) regulations, it will make it very difficult to protect the coating system from corrosion and loss of adhesion especially on the aluminum primer surface and interfaces. Furthermore, chromium base inhibitor is used for chemical conversion coating at the

aluminum surface. In addition, chromium base inhibitor is used within the primer coatings. Major efforts are being devoted for replacement of the chromium inhibitor in the coating system.

The source of coating system degradation is not only known because of corrosion and loss of adhesion, but due to photo-oxidation processes taking place as a result of exposing the system to weathering conditions, various service conditions, as well as to UV irradiation. To eliminate the damage to the polymer coating, pigments, and stabilizers are being introduced into the coating. These compounds will absorb the UV as well as the free radicals. Under these conditions the system could be protected against corrosion and adhesion loss by using new non-chromate base solution and by using pigments into the coating to protect it against photo-oxidation processes resulting from UV irradiation.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 12, Coating System Formation, Degradation, and Stabilization Survey.

TASK: 43

TASK TITLE: NDE and Aging Systems Technology Transition Development

TASK OBJECTIVE: Identify, analyze, and/or develop enhanced methods for technology transition of sonic, electromagnetic, radiographic, and optical methodologies for use in nondestructive evaluation (NDE) and in aging systems.

SCIENTIST: Matthew J. Golis, Ph.D., Advanced Quality Concepts

DESCRIPTION OF WORK:

This project provided assistance in the development of enhanced methods for technology transition of Nondestructive Evaluation (NDE) technologies between the private sector and the Wright Laboratory. A special emphasis was placed on matters relating to the aging systems within the U.S. Air Force. Project activities centered around expanded presentations of weep-hole crack sensor inspection results, conferring on NDE technology issues and assisting in creating links

between the branch's technical staff and private industry involved in aircraft component manufacture and repair.

Participation in several technology conferences took place in order to bring the activities of the NDE Branch to the attention of other branches of the USAF community and the private commercial sector. Presentations on the advancements made in weephole inspection using a novel ultrasonic creeping-wave technique were made at both the 3rd Air Force Conference on Aging Aircraft and the 1995 USAF Structural Integrity Program Conference. Sessions on aircraft-related NDE at the Fall Conference of the American Society for Nondestructive Testing (ASNT) were attended as well as the semi-annual meeting of the ASNT Aerospace Committee.

The report recommends ways in which the Air Force NDE technologies can be transitioned to both the private sector and other agencies based on continued close interactions with key individuals active in the NDE field including manufacturers of aircraft components and systems.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 23, NDE and Aging Systems Technology Transition Development.

TASK: 44

TASK TITLE: The Analysis of Creep/Fatigue Damage in Oxide/Oxide Composites

TASK OBJECTIVE: To identify and document the development of damage in an oxide/oxide ceramic matrix composite under combined creep and fatigue loading.

SCIENTIST: Shin S. Lee, Ph.D.

DESCRIPTION OF WORK:

Cyclic deformation in brittle matrix composites at room temperature environment, in general, is attributed to damage development, such as opening of matrix cracks fiber breakage. At elevated temperature environments, cyclic deformation may be induced by creep deformation and greatly affect fatigue performance, especially in fiber dominated systems. Such creep related deformation

observed in high temperature tension fatigue test becomes doubly critical in high stress ratio fatigue tests. In the present investigation, the influence of creep induced reduction of fatigue performance was investigated in a newly developed polycrystalline fiber dominated CMC system.

Several different R ratio T-T fatigue tests were conducted at 1000°C to characterize the influence of creep on cyclic deformation. In addition, fatigue tests with different loading frequency and hold time were also investigated.

The material used for the investigation was GEN-IV which contains Nextel 610 fiber and Alumino Silicate matrix without fiber coating and matrix filler. The system has 2-D 8-harness satin weave structure. Fatigue tests were conducted under load control with 0.05 load ratio ($s_{min}/s_{max}$) and 1 Hz frequency at 1000°C. Two different load ratios, 0.2 and 0.6, were also selected for the 1000°C fatigue tests. The maximum stress was 75 MPa and 125 MPa for fatigue tests. Creep rupture tests were also conducted under load control. The run out condition for 1000°C fatigue, and creep rupture tests were $10^5$ cycles and 100 hours, respectively. The creep tests were conducted at the same stress levels for the fatigue tests.

The mean stress of the fatigue test conducted at R=0.6 (75/125) was 100 MPa; and the life of such test was 24665 cycles which equals to 24665 seconds. The life of the creep rupture test conducted at 100 MPa was 22345 seconds which is close to the life of the fatigue test with the mean stress equal to 100 MPa. Similar test conducted at R=0.2 (25/125) exhibits a great improvement of fatigue performance. The mean stress of R=0.2 was 75 MPa which is also the highest run out stress obtained in the creep rupture tests. The influence of R ratio, or mean stress, on the fatigue performance of GEN-IV was confirmed, based on the investigation.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 15, High Temperature Cyclic Deformation.

TASK: 45

TASK TITLE: Thermomechanical Fatigue of Oxide/Oxide Composites

TASK OBJECTIVE: To identify and document the development of damage in an oxide/oxide ceramic matrix composite under combined thermal and mechanical loading.

SCIENTIST: Shin S. Lee, Ph.D.

DESCRIPTION OF TASK:

A modern ceramic matrix composite (CMC) was extensively characterized for a high-temperature aerospace application. The CMC system has a Si-N-C matrix reinforced with Nicalon fibers woven in a balanced eight harness satin weave (8HSW) fabric. Tensile tests demonstrated that this CMC exhibits excellent tensile strength retention up to 1100°C. The room-temperature fatigue limit was found to be 160 MPa and is approximately 80% of the room-temperature tensile strength. An improved long-term performance under cyclic tensile loading was observed at stress levels above the proportional limits at 1000°C in air. In addition, the composite exhibits remarkable high-temperature durability under sustained tension at a stress of ~ 35 MPa above the proportional limit at temperatures up to 1100°C. In comparing the 1000°C creep rupture data with 1000°C fatigue data on a time basis, it was found that cyclic loading caused a significant reduction in long-term performance. Accelerated degradation was observed in the 1000°C fatigue specimens that were periodically removed from the test machine and exposed to a salt-fog environment. This degradation decreased the fatigue life approximately 85% for the stress levels tested. The CMC system studied in this program was manufactured by Kaiser Ceramic Composites.

Microanalysis of the fiber-matrix interface was conducted on as-received material using a fiber push-in technique. The push-in probe used in these experiments had a ground conical diamond tip with a 55° included angle and a 10 μm flat. All of the interface data was collected at room temperature using the Micro Measure Machine designed specifically for fiber interface testing. The recorded raw data from each test included the load applied to the fiber during push-in as well as the displacement, both as a function of time.

The mechanical behavior tests were conducted on a horizontal servohydraulic machine using water cooled rigid hydraulic clamping grips and quartz lamp heating. Test control, data acquisition, and interactive data analysis functions were provided by the MATE Program installed on an IBM-compatible personal computer that was linked to the test frame via an analog-to-digital board. Temperature was measured by bonding five "S" type thermocouples to each specimen using an

alumna-based ceramic adhesive. The specimen design was a reduced gage section "dogbone" specimen.

Room-temperature, 1000°C, and 1100°C, tension tests were conducted under stroke control with a constant displacement rate of 0.05 mm/sec. Residual strength tests were also conducted on all specimens that reached run-out during creep rupture and fatigue testing.

Fatigue tests were conducted under load control with a stress ratio of 0.05. The maximum applied stress levels for the fatigue tests were selected to be both below and above the proportional limits determined from the tension tests to determine the role of matrix cracking on room-temperature and high-temperature fatigue performance. The room-temperature tests were allowed to run for $10^6$ cycles. The room-temperature tests were cycled at a frequency of 1 Hz for the first 100,000 cycles and then at 5 Hz for an additional 900,000 cycles or until failure.

Creep rupture tests were conducted under load control at 1000°C and 1100°C. A high-temperature extensometer with alumna rods was used to measure creep strain. The applied stress levels were selected to be both below and above the proportional limit determined from the high-temperature tension tests. Creep strain was recorded from the instant the specimen reached the test stress level.

To study environmental degradation CMC specimens were exposed to salt-fog in a cyclic corrosion chamber. The NaCl salt concentration was 0.05 $^{w}/_{o}$. A concentration of 5 $^{w}/_{o}$, as typically used in corrosion studies on marine paints, was considered a worst case condition and evaluated for two tests. The specimens were fatigued for 5000 cycles and then exposed to salt fog for 24 hours.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 61, High-Temperature Performance of Fiber Reinforced Ceramic Matrix Composites.

TASK: 46

TASK TITLE: Effects of Processing Parameters on the Morphology and Mechanical Characteristics of Microcellular Graphitic Foams

TASK OBJECTIVE: To process graphitic microcellular foams under different processing conditions and study the effects of processing variables on foam morphology and properties.

SCIENTIST: Debashis Dutta, Ph.D., Wright Materials Research

DESCRIPTION OF WORK:

In this effort research was performed on processing and characterization of graphitic microcellular foams from mesophase pitch. It has been predicted that foams with interconnected strut networks of aligned graphite crystallites will have attractive mechanical properties. It was demonstrated in the previous report that graphitic foams with the desired morphology can be processed with homogeneous nucleation techniques. But, the properties could not be evaluated as the sample sizes were very small. A larger foaming device was fabricated and used to process larger foam samples.

The effect of different processing parameters on foam morphology and properties were evaluated. The objective was to identify the processing window for foaming of AR pitch. The variables studied were sample thickness, saturation pressure, foaming temperature, and quenching mechanism. It was observed that cell density increased with increasing pressure. This was consistent with predictions from nucleation theory. Sample thickness also affected the foam morphology. The thicker samples had lower bubble density. This could be due to poor gas solubility in the thick parts. Preliminary mechanical tests showed that, in general, the foams were 30-40% stiffer than carbonized amorphous foams. Attempts were also made to process in-situ sandwich structures with carbon fiber fabric as the outer layers.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 45, Processing and Characterization of Graphitic Microcellular Foams from Mesophase Pitch.

TASK: 47

TASK TITLE: Self-Lubricating Composite Coatings for Extreme Environments

TASK OBJECTIVE: Development of composite coatings comprised of solid lubricant, ceramic, and metallic phases.

SCIENTIST: Somuri V. Prasad, Ph.D.

DESCRIPTION OF WORK:

This project involved the development of tribological coatings for extreme environments. The role of a tailored metal-matrix composite (MMC) in imparting improved tribological behavior to tungsten disulfide ($WS_2$) films in humid air was investigated in the first part. As a result of tribo-oxidation, tungsten disulfide loses its lubricating characteristics in humid environments; by enabling the diffusion of gaseous species along the crack front, crack propagation further enhances the rate of tribo-oxidation. In the current study, tungsten disulfide films were grown onto tailored MMC substrates with silicon carbide protrusions by pulsed laser deposition (PLD). Friction measurements were made in dry nitrogen and humid air with 90 %RH. Analyses of the wear surfaces showed that at several instances, carbide protrusions on the MMC substrate either arrested or deflected a propagating crack front. In humid air, the films on MMC substrates were found to have prolonged wear life with friction coefficients less than 0.2, while the films on polished steel substrates failed almost instantly. The second part of the project was addressed to the development of lubricious oxide coatings. Substoichiometric nanocrystalline zinc oxide (ZnO) films were grown onto steel substrates by PLD. Substrate temperature and oxygen partial pressure were varied to grow films with different stoichiometries and grain sizes. The friction coefficient of a conventional hot pressed ZnO disk was high, 0.65; the steel counterface after wear testing was full of scratches. By contrast, the friction coefficients of PLD ZnO films were between 0.16 and 0.34; the steel counterface after testing was practically free of any scratches. Extensive plastic deformation of ZnO was observed on the wear scars. The improved tribological performance of the PLD ZnO films was attributed to their nanocrystalline grain structure and oxygen substoichiometry.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume Volume 59, Lubricious Coatings for Extreme Conditions.

TASK: 48

TASK TITLE: Evaluation of Turbine Engine Tested Ceramic Matrix Composite Components

TASK OBJECTIVE: To identify and document the performance of four different ceramic matrix composite systems that have been engine tested in an F110 turbine engine.

SCIENTIST: James M. Staehler, M.S.

DESCRIPTION OF WORK:

This effort was broken into two tasks, each with its own scope and purpose. However, an underlying objective common to each was the evaluation of composite materials for possible use in turbine engine exhaust nozzles. In Task 1 a silicon nitride-boron nitride fibrous monolith was considered. Preliminary data from a room temperature monotonic tensile test and a 1000C tensile creep test were collected. The material has a very high room temperature tensile strength of 350 MPa with a linear stress-strain response to failure. It survived the 100 hour, 150 MPa creep test without loss of room temperature properties although it did show evidence of oxidation at the exposed surfaces. Task 2 evaluated the residual tensile strength data collected on a Nextel 720 fiber reinforced aluminosilicate panel subjected to thermal gradient testing. The survivability of the material on an exhaust nozzle due to thermally induced stresses was of concern. The gradients were simulated in the laboratory and later the panel was cut into tensile specimens. One obvious crack was noted in the panel. A second became apparent as a result of the residual strength tests. The material is susceptible to thermal gradients and cracks can form as a result of the corresponding thermal stresses. The damage does appear to be somewhat limited and localized.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume Composite Material Evaluations.

TASK: 49

TASK TITLE: Indium Phosphide Based Single Quantum Wells

TASK OBJECTIVE: Evaluate the electronic properties of quantum wells grown by molecular beam epitaxy and metal-organic chemical vapor deposition on indium phosphide substrates with indium gallium arsenide wells and determine the effects of varying barrier materials.

SCIENTIST: Mohamed Ahoujja, University of Cincinnati

DESCRIPTION OF WORK:

In this project electronic transport properties of d-doped InGaAs/AlAsSb heterostrutures lattice-matched to InP substrate were investigated using temperature dependence of the Shubnikov-de Haas oscillations and Hall effect measurements. The basic properties, including the electron mobility and carrier concentration of the two-dimensional electron gas embedded in the InGaAs well were determined. The concept and effect of d-doping on the electrical properties of heterostructures was discussed. The carrier concentration in the well is so high that both the first and second electric subbands are populated. Illumination increased the carrier density from 26.73 to 28.20 x $10^{11}$ $cm^{-2}$ and from 6.61 to 7.20 x $10^{11}$ $cm^{-2}$ in the first and second subband respectively. The increase in the carrier density is attributed to the photo excitation of deep defects in the AlAsSb barrier.

The Hall mobility, as well as the electron mobilities in the two subbands, increased with carrier concentration. The mobility in the second subband was found to be higher than that in the first subband in agreement with published reports on semiconductor heterostructures.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 40, Magnetotransport Properties of d-doped AlAsSb/InGaAs Heterostructures.

TASK: 50

TASK TITLE: Deep Levels in Silicon Carbide

TASK OBJECTIVE: Determine the effect of polytype on the deep levels present in bulk grown silicon carbide wafers and evaluate possible dopants for the formation of semi-insulating SiC.

SCIENTIST: Andrew O. Evwaraye, Ph.D.

DESCRIPTION OF WORK:

Bulk silicon carbide of different polytypes (4H-, 6H-, and 15R) grown under different conditions by physical vapor transport (PVT) were studied using capacitance-voltage measurements, thermal admittance spectroscopy, optical admittance spectroscopy and high temperature Hall effect measurements. Using Ag, Al, Au, and W as metal contacts the barrier heights for these metals were determined as functions of temperature.

The nitrogen levels in n-type 4H-SiC were determined to be at $E_C$ - 0.053 eV and at $E_C$ - 0.1 eV. The $E_C$ - 0.1 level is associated with Nitrogen atoms occupying the cubic sites. The boron level in p-type 6H-SiC was also determined; its activation energy ranges from $E_V$ + 0.28 eV to $E_V$ + 0.35 eV. It appears to depend on the background doping and compensation.

Optical admittance studies of both 6H- and 4H-SiC were carried out. From these studies, the band gaps of 4H and 6H-SiC were precisely determined. It is 3.10 eV for 6H-SiC 3.41 eV for 4H-SiC. The behavior of the vanadium donor in 4H-SiC was compared to the vanadium donor in 6H-SiC. The positions of the vanadium donor in 4H- and 6H-SiC were used as reference to predict the band alignment of 4H-SiC/6H-SiC heterojunction.

The thermal activation energy $e_3$ for hopping in heavily doped 4H-SiC was determined to be 3.29 meV. This was compared with the value obtained from resistivity versus temperature measurements.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 53, Electrical and Optical Characterization of Bulk Silicon Carbide.

TASK: 51

TASK TITLE: Investigations of Fracture in Intermetallics Alloys

TASK OBJECTIVE: Explore new theories of the ductile-brittle transition and fracture initiation in intermetallic alloys via a combined theory and experimental approach.

SCIENTIST: Yong Qian Sun, Ph.D.

DESCRIPTION OF WORK:

This project consisted of two parts. Part-I, the main part, consisted of brittle-to-ductile transition and the experiments on single crystal intermetallic NiAl. Part-II consisted of theoretical investigation of the microstructure-property relationship of intermetallic TiAl-based alloys.

In Part-I, single crystals of NiAl in the [001] orientation were prepared into wire tensile specimens and tested in tension over a temperature range (room temperature to 314°C) that included the brittle-to-ductile transition. The specimens exhibited a sharp brittle-to-ductile transition at about 229°C. The deformation in the ductile region was characterized by a well defined yield point and a large yield drop. The yield stress near the transition temperature was around 1200 MPa.

Simultaneously with the tensile tests, in Part-II changes in the specimens' electrical resistance were measured as a means to probe dynamically the dislocation formation and evolution under high stresses. The electrical resistance ($R$) increased linearly with elongation ($L$), but at different rates ($dR/dL$) in the elastic and plastic regions of the deformation, with the rate in the plastic region being 2.4 to 3.0 times as large as that in the elastic region. $dR/dL$ exhibited an abrupt jump at the yield point and correlated sensitively with the flow stress, but was approximately invariant with the total plastic strain. The differences in $dR/dL$ in the elastic and plastic regimes were shown to be unrelated with the differing specimen shape changes in these two regimes, but to represent different

electrical resistivity values of the undeformed specimen ($\rho_E$) and the specimen sections actually undergoing plastic deformation ($\rho p$); namely $\rho p$ was larger than $\rho_E$ by a factor of 2.4 to 3.0. The abruptness of the electrical resistivity increase at the onset of plastic deformation was interpreted to result from the abrupt formation of dislocations, the total density of which depended sensitively on the flow stress but was independent of the total plastic strain.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 79, The Brittle-to-Ductile Transition of [001] NiAl Monitored by Electrical Resitivity and the Collective Nucleation of Dislocation Loops Under Near-Failure Stresses.

TASK: 52

TASK TITLE: Project Management/Administration

TASK OBJECTIVE: To provide support activities necessary to establish project task orders and overall contract administration.

SCIENTIST: Milton E. Zellmer

DESCRIPTION OF WORK:

The contributive research and development project required extensive management and administration activities that were not readily charged to a specific task. These activities fell into three general categories:

1. Those contract management administrative requirements to establish planning and control procedures that applied to the project as a whole. Examples are status reporting, project management meetings, and other general overall project reporting.

2. Those management activities required to establish each of the task assignments. These activities could not be charged to the task since the task was not yet approved during this phase.

3. Recording and reporting the performance and cost for the overall management and administrative activities.

This task provided project management/administration from 16 December 1995 through 15 December 1996.

TASK: 53

TASK TITLE: Ceramic Composite Characterization

TASK OBJECTIVE: To characterize ceramic fiber-matrix composites and their constituents by optical microscopy, scanning electron microscopy, and transmission electron microscopy for phase abundance and microstructures. To characterize the fiber-matrix interface and correlate with mechanical properties.

SCIENTIST: Rajagopalan Nagarajan, Ph.D.

DESCRIPTION OF WORK:

The research work involved primarily characterizing the coating on the Nextel 720 fibers in the ceramic matrix composites and Alumina/YAG eutectic ceramic samples using analytical electron microscopic techniques. The samples were characterized using conventional electron microscopic techniques and energy dispersive x-ray spectroscopy (EDS) and parallel electron energy loss spectroscopy (EELS) techniques.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 197, Ceramic Composite Characterization.

TASK: 54

TASK TITLE: Thermomechanical Fatigue and Environmental Effects in Titanium Intermetallics and Composites

TASK OBJECTIVE: To develop an understanding of the role of environment in isothermal and thermomechanical fatigue of gamma titanium aluminides and titanium alloys and their composites.

SCIENTIST: Andrew H. Rosenberger, Ph.D.

DESCRIPTION OF WORK:

Several areas of research were performed that pertained to determining the mechanical modes of damage or environmental attack that affect the mechanical performance of high temperature structural materials. The first area was the completion of the first phase of an examination of the environmental effects on the fatigue crack growth behavior of gamma titanium aluminides. Here, the data set was completed for two different microstructures of alloy K5 in the duplex and nearly fully lamellar microstructural conditions. Some interesting experimental observations were made concerning fracture surface roughness measurements.

The second and third areas of research were the examination of the behavior of SCS-6/Ti-6Al-4V composites in $[0]_8$ and $[90]_8$ layups, respectively. Here the thermomechanical fatigue behavior of $[0]_8$ and the isothermal fatigue of the $[90]_8$ were experimentally explored and a number of observations regarding the damage mechanisms were made.

The fourth area of research was an examination of the effectiveness of a $TiAl_3$ + glass coating as a protective system capable of enhancing the life of a metal matrix composite. A number of SCS-6/Ti-22Al-23Nb $[0]_4$ composite specimens were coated with the above experimental protective system and subjected to isothermal and thermomechanical fatigue with a maximum temperature of 650°C. No protection was offered by the coating system and possible reasons for this were discussed.

The final area was a comparison of the mechanical performance of Trimarc-1/Ti-22Al-23Nb $[0]_4$ and Trimarc-1/Ti-25Al-17Nb-1Mo $[0]_4$ composites with the baseline SCS-6/Ti-22Al-23Nb $[0]_4$ composite. The lower strength Trimarc-1 fiber offers no improvement in performance compared to the SCS-6 fiber.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 52, Mechanical Damage Modes and Environmental Attack in Titanium Aluminides and Titanium Matrix Composites.

TASK: 55

TASK TITLE: Infrared Optical Power Limiter Research

TASK OBJECTIVE: Materials characterization, device development, and system integration of infrared optical power limiters.

SCIENTIST: Shekhar Guha, Ph.D.

DESCRIPTION OF WORK:

The objective of this work was to characterize infrared optical materials and develop infrared optical power limiter devices for their eventual integration into optical systems. In 1996, a new in-house capability for characterization of the optical properties of materials was developed at Wright Laboratory (WL/MLPJ). Several novel materials were characterized in detail and their usefulness for infrared optical power limiting was demonstrated. A nonlinear optical beam propagation code was developed for use in the integration of the devices developed into optical systems.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume Volume 64, Infrared Optical Power Limiter Research.

TASK: 56

TASK TITLE: Development of Predictive Tools for High Order (3+ Element) Compounds

TASK OBJECTIVE: To investigate the feasibility of using heuristic methods to design electro-optic materials for threat and/or detection applications.

SCIENTIST: Jack Park, ThinkAlong Software, Inc.

DESCRIPTION OF WORK:

A survey was made of the background issues relatedto the construction of models and theories which will support the design and manufacture of new aerospace materials. This research focused on those issues as related to a class of materials with specific electro-optical properties, the Chalcopyrites. It is seen that an important background issue is that of the mapping of continuous, real-valued attributes to a discrete space. This mapping is required for the development of suitable models to be used in materials properties analysis.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 55, Towards a Roadmap for Materials Design.

TASK: 57

TASK TITLE: Theoretical Study of III-V Molecular Beam Epitaxy Growth Mechanisms

TASK OBJECTIVE: Develop computer models that accurately predict the stoichiometry and surface/interface morphology of III-V thin films.

SCIENTIST: Krishnamurthy Mahalingam, Ph.D.

DESCRIPTION OF WORK:

In-situ desorption mass spectroscopy studies (DMS) of AlGaAs/GaAs molecular beam epitaxy (MBE) at high substrate temperatures reveals a rich transient behavior in the Ga desorption signal during the formation of the AlGaAs-on-GaAs interface. In this study, Monte Carlo (MC) models for Ga desorption were developed, in which the effects of the Al-Ga interaction strength and the inclusion of an Al-Ga surface exchange mechanism were investigated. The models which best describe the experimental observations were identified. The transients in Ga desorption rate at the AlGaAs-on-GaAs interface and the experimentally observed reduction in Ga desorption energy during growth of AlGaAs were explained in terms of the reduction in V/III flux ratio accompanying the opening of the Al shutter. The proposed effects of this reduction in V/III flux ratio are consistent with the results predicted by the different models. MC simulations employing a constant V/III flux ratio yield a "step-like" variation in the Ga desorption rate with the resulting interfaces

closer in abruptness to the ideal AlGaAs-on-GaAs interface. Details on the stoichiometry of the interface and its relationship with predicted Ga desorption profiles were presented.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 68, Gallium Desorption Behavior at AlGaAs/GaAs Heterointerfaces during High-Temperature Molecular Beam Epitaxy.

TASK: 58

TASK TITLE: Investigation of Advanced Metallic Composites II

TASK OBJECTIVE: To develop an understanding of the relationships between the composition and microstructure of matrices, the bonding at fiber/matrix interfaces, and composite properties in advanced metallic composites.

SCIENTIST: Sunil G. Warrier, Ph.D.

DESCRIPTION OF WORK:

The objective of this research task was to develop a fundamental understanding of the role of interface properties on the deformation behavior of continuous fiber-reinforced titanium matrix composites. Two aspects of deformation were studied in this task. One, determining the stress distribution during torsion tests in an effort to identify the failure mechanism during transverse loading, and two, examining the influence of interface properties on the fatigue crack growth behavior of composites.

It was observed from finite element analysis that the tangential shear stress supported by the interface at the onset of non-linearity in the strain vs the angle of twist curve during torsion testing was of the order of 50 MPa for SCS-6/Ti-6Al-4V composites, 40 MPa for AC1/Ti-6Al-4V composites and greater than 80 MPa for SCS-0/Ti-6Al-4V composites. Based on these results and comparison with experimental observations and finite element analysis of transverse tension tests, the failure mode in SCS-6/Ti-6Al-4V and AC1/Ti-6Al-4V composite during transverse loading appears to be influenced by the tangential shear failure of the interface. In SCS-0/Ti-6Al-4V composites, results are not conclusive.

The influence of interface properties on the fatigue crack growth behavior of composites was investigated. Data from the experiments conducted in the previous research task was included in the analyses. The shielding effect as the crack approaches the fiber was seen to vary as a function of the coating/interfacial bond strength. The crack growth rate as the crack approached the fiber was about four times in the case of yttrium coated SCS-0/Ti-6Al-4V composites compared to that in SCS-0/Ti-6Al-4V composites.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 27, Effect of Interfacial Properties on the Deformation Behavior of SiC/Ti-6Al-4V Composites.

TASK: 59

TASK TITLE: Reaction Kinetics of Halon and Halon Replacements

TASK OBJECTIVE: To develop a fundamental understanding of the chemical mechanisms of Halon fire suppressant action through computational chemistry. To use this understanding to evaluate alternative compounds presently being considered, and other completely different compounds, for fire suppressant capability.

SCIENTIST: Rajiv J. Berry, Ph.D.

DESCRIPTION OF WORK:

The thermochemistry and reaction kinetics of halogenated hydrocarbons were investigated by *ab initio* methods in order to improve understanding of their flame chemistry and likely roles in flame suppression. Bond additivity corrections at the G2, G2(MP2), CBS-4 and CBS-Q levels of theory were developed for fluorinated and chlorinated $C_1$ and $C_2$ species, including saturated and unsaturated compounds. The resulting enthalpies of formation were in excellent agreement with experimental values. Transition states for the reactions of H atoms with hydrofluoromethanes were characterized at up to the G2 level of theory, and application of transition state theory yielded rate constants in good agreement with experimental results. A similar analysis for H and OH reactions with $CH_3I$ also agreed with the known thermochemistry and kinetics. These investigations

provided insight into the major product channels and the temperature dependence of the rate constants. The implications for flame suppression by haloalkanes were discussed.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 67, *Ab Initio* Calculations for Kinetics Modeling of Halocarbons.

TASK: 60

TASK TITLE: Deformation Mechanisms in Gamma Titanium Aluminides

TASK OBJECTIVE: The objective of the task is to analyze, characterize, and understand the fundamental deformation behavior in gamma titanium aluminides.

SCIENTIST: Sriram Seshagiri, Ph.D.

DESCRIPTION OF WORK:

The work accomplished in this project consisted of two parts. Part I investigated the geometry and nature of pinning points of 1/2<110] unit dislocations in binary TiAl alloys, and Part II investigated the statistical distribution of lamellae variables in fully lamellar polycrystalline TiAl alloys. The work accomplished in Part I showed that the b=1/2<100] unit dislocations in deformed TiAl alloys exhibited a unique morphology, consisting of numerous pinning points along the dislocation line aligned roughly along the screw dislocation discretion, and bowed out segments between the pinning points. The three dimensional arrangement of these dislocations had been characterized in detail, based on *post-mortem* weak-beam TEM observations in deformed binary Ti-50Al and Ti-52Al alloys. The bowed segments glide on parallel {111} primary planes, and the pinning points are jogs with a range of heights, up to a maximum of ~40nm. The substructure evolution was consistent with dislocation glide involving frequent *double cross-slip* and consequent jog formation. The dislocations experienced a large glide resistance during the forward (non-conservative) motion of these jogs. Pinning of unit dislocations experienced is an intrinsic process in these alloys, and is not related to the presence of interstitial-containing precipitates in the matrix. The temperature dependent increase in the linear pinning point density is not very sensititive to alloy composition. An outline of a flow-stress model was developed, based on a single dislocation

experiencing a spectrum of resisting forces resulting from a range of jog heights; the shorter jogs contributed to glide-resistance via friction, and the taller ones via a dipole-dragging mechanism. Estimates of the resisting force due to both these processes were shown to account for the measured flow-stress reasonably well.

Work accomplished in Part II showed that the microstructural variables, namely the thickness of the $\alpha 2$ (A) and $\gamma$ (G) lamellae, the spacing between the $\alpha 2$ lamellae (S) and the characteristic spacing ($\lambda$) between them, followed a log-normal distribution. Systematic changes in the mean value of these parameters were observed with changes in the cooling rates. In general, the increasing cooling rates led to finer lamellae spacings and thicknesses. Concomitantly, the volume fraction of $\alpha 2$ also changed, and was sensitive to the cooling rates employed. The yield strength in fully lamellar polycrystalline TiAl alloys was intimately associated with these changes in the microstructural parameters. It was shown that a Hall-Petch (HP) type correlation existed between $\lambda$ and S, with a better correlation coefficient for the former.

The detailed project description, method, results and discussion are reported in Contributive Research and Development Final Report, Volume 70, Deformation Behavior and Dislocation Mechanisms in TiAl Alloys.

TASK: 61

TASK TITLE: Develop and Implement Compatible Data Collection for Surface Analysis Equipment

TASK OBJECTIVE: To develop data collection and manipulation capabilities and implement them on existing surface analytical equipment.

SCIENTIST: Donald Thomas, M.S.

DESCRIPTION OF WORK:

The Surface Interactions Group of the Air Force Wright Laboratory's MLBM division operates a number of surface analysis systems. Each of these systems support one or more of the following analysis techniques:

- Auger electron spectroscopy (AES)
- X-ray photoelectron spectroscopy (XPS)
- Secondary-ion mass spectroscopy (SIMS)
- Ion-scattering spectroscopy (ISS)

This research project was an attempt to create a compatible data collection system that supports each of these techniques on each surface analysis system and will meet the following goals:

- Present a common interface across each of the surface analysis systems and across each of the analysis techniques.
- Create a modern, graphical-user interface, which is intuitive and easy to use.
- Allow exporting of data to a standard file format which can be imported into various third-party data processing software.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 41, Development of a Compatible Data Collection and Analysis System.

TASK: 62

TASK TITLE: Experimental Nondestructive Evaluation (NDE)

TASK OBJECTIVE: Analyze material response to ultrasonic excitation for the characterization of advanced materials and processes.

SCIENTIST: Peter B. Nagy, Ph.D.

DESCRIPTION OF WORK:

The main objective of this research was to further develop the ultrasonic creeping wave inspection technique to detect radial fatigue cracks in thin stiffeners containing circular "weep" holes. Often these cracks are located on the inner part of the weep hole where they are hidden from

the outer skin. Such cracks are not readily detected by conventional ultrasonic inspection techniques therefore a special method based on circumferential creeping waves was adapted. In the case of 0.25"-diameter weep holes, fatigue cracks as small as 3 mils could be detected at 5 MHz. Although this threshold sensitivity is more than sufficient for field inspection, the wet wing has to be emptied and dried out before inspection because even a small amount of fluid fuel trapped in these rather small holes would strongly affect the propagation of circumferential creeping waves.

The current effort was directed at developing the analytical techniques needed to optimize the inspection technique for fluid-filled weep holes. The dispersion equation for circumferential creeping waves around a fluid-filled cylindrical cavity in an infinite elastic medium was derived by satisfying the appropriate boundary conditions at the interface. Phase and group velocity as well as attenuation curves were constructed by numerically solving this dispersion equation. A comparison of the corresponding modes for elastic and rigid hosts is presented. The modes in both cases exhibit essentially the same series of cutoff frequencies corresponding to radial resonances at which the phase velocity of the associated modes becomes infinite and the group velocity assumes a constant limiting value. Attenuation of the circumferential creeping modes in a cylindrical cavity is caused solely by losing energy to the surrounding elastic bulk. Therefore, for all modes, the attenuation diminishes at high-frequencies as leakage into the surrounding solid becomes negligible. This is in sharp contrast with the case of leaky Rayleigh wave propagation along the plane surface of a solid-fluid interface when attenuation is caused solely by radiation of energy into the fluid, which causes the frequency to have an opposite effect on the degree of leakage in these situations.

In broadband ultrasonic experiments, two main types of circumferential waves can propagate along a fluid-filled weep hole, namely whispering gallery modes that carry most of their energy in the fluid and Rayleigh-type mode that propagates essentially in the solid. Although the Rayleigh mode turns out to be the weaker one of the two modes, it is the only one that can be used to inspect the near-surface region of the solid for cracks and other defects, therefore it is the more important one from a nondestructive testing point of view.

The detailed project description, method, results and discussion are reported in Contributive Research and Development Final Report, Volume 62, Circumferential Creeping Wave Inspection of Fluid-Filled Weep Holes.

TASK: 63

TASK TITLE: Ceramer Technology

TASK OBJECTIVE: Synthesis of high performance polymers amenable to state-of-the-art sol-gel processing.

SCIENTIST: Narayanan Venkatasubramanian, Ph.D.

DESCRIPTION OF WORK:

Thermoplastic resins with sulfonic acid pendants have potential utility as transparent host matrix for monodispersion of second order NLO chromophores via ionic association between the sulfonic acid functionality of the matrix and the pyridyl or N,N-dialkylamino functionality of the NLO chromophore. New high molecular weight sulfo-pendent aryletherketone homopolymers and copolymers were utilized for obtaining electro-optic guest-host systems incorporating aromatic heterocyclic chromophores with pyridyl base functionailty or the more commonly known NLO chromophores containing donor N,N-dialkylamino base functionality. Polymer film compositions incorporating the aromatic heterocyclic chromophores, especially 1-(4-pyridyl)-2-(2-thienyl)ethene (PTE) and 1-(4-pyridyl)-2-[5-(2,2′-bithienyl)ethene (thienyl PTE) were obtained with high optical transparency and homogeneity. Examination of the NLO guest-host polymer morphology by WAXD and SEM confirmed the monodispersed nature of the films. However, mixed results were obtained for NLO chromophores with an N,N-dialkylamino donor and nitro group terminal acceptor. Among the chromophores examined, an optically clear film composition was obained only in the case of 1-(4-N,N-diethylaminophenyl)-2-nitroethane (DEANST) in the sulfonated copolymer matrix. The significance of the acid-base interaction mediated guest-host systems stems from the demonstrated potential in this study, for obtaining much higher chromophore loadings in the matrix polymers without phase separation compared to conventional guest-host electro-optic polymer systems.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 69, Poly(arylene ether ketones) with Sulfonic Acid Pendants-Transparent Polymer Hosts for Second Order NLO Chromophores.

TASK: 64

TASK TITLE: Molecular Beam Epitaxy

TASK OBJECTIVE: Develop and apply techniques for molecular beam epitaxial (MBE) growth of strained layer superlattice materials for applications such as, but not limited to, long wave length infrared detector and nonlinear optical materials.

SCIENTIST: J. Ken Patterson, Ph.D.

DESCRIPTION OF WORK:

Conventional elemental source Molecular Beam Epitaxy (MBE) was used for the growth of thin film crystals of InAs, GaSb, and AlSb as well as preparing fresh surfaces of these crystals. Crystal growth conditions were monitored by Reflection High Energy Electron Diffraction (RHEED), and specifically prepared surfaces were analyzed with Ion Scattering Spectroscopy (ISS). The choice of ISS probe gas (He or Ne) was seen to greatly affect the InAs sample surface composition due to the incident probe beam itself. Adventitious contamination of MBE grown InAs, GaSb, and AlSb films was analyzed by Secondary Ion Mass Spectrometry (SIMS), and no alarming amounts of contamination were seen. However, significant interdiffusion of group V elements was seen to occur for an AlSb layer sandwiched between InAs and GaAs.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 35, Growth and Studies of InAs, GaSb, and AlSb MBE Single Crystal Surfaces and Thin Films.

TASK: 65

TASK TITLE: Corrosion Prevention Technology for Advanced Aircraft Coatings Systems

TASK OBJECTIVE: The Air Force requires development of Paint For Life Aircraft Coatings Systems which provide corrosion protection for aircraft surfaces throughout the life of aircraft. The objective of this task is to develop enabling corrosion prevention materials and processing technology for the new coatings systems. This corrosion prevention technology is based on a thorough, fundamental understanding of corrosion phenomenon as related to aircraft systems, and includes corrosion inhibitor mechanisms. The corrosion prevention technology will be incorporated into aircraft coatings systems beyond the year 2003.

SCIENTIST: Mohammed Khobaib, Ph.D., University of Dayton Research Institute

DESCRIPTION OF WORK:

This research was a part of the U.S. Air Force "Paint for Life Aircraft Coatings Systems" program which aims to provide corrosion protection to aircraft surfaces throughout the life of aircraft. The objective of this study was to conduct hands-on, inhouse research to better understand the corrosion-related problems faced during the development stage of new advanced coatings systems. The study included the development of a thorough and fundamental understanding of the corrosion phenomenon as related to aircraft systems, including the mechanism of corrosion inhibition.

The corrosion-prevention behavior of a number of coatings currently used by the U.S. Air Force was studied employing modern electrochemical techniques including the Electrochemical Impedance Spectroscopy (EIS) and the Electrochemical Noise Method (ENM). EIS and ENM were also used to understand the mechanism of corrosion prevention offered through a selected number of coatings being developed by the U.S. Air Force under High Performance Advanced Aircraft Coatings program.

Sol-gel films were being investigated as potential replacements for chromate-based surface treatments for high-strength aluminum alloys. The corrosion-resistance behavior of a large number of Sol-gel chemistries, with or without inhibitor dopings, was also investigated. The analysis of potentiodynamic anodic polarization scans provided initial basic understanding of the corrosion behavior of these films. The films, which showed good corrosion resistance, were later analyzed through EIS testing.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 81, Corrosion Prevention Technology for Advanced Aircraft Coating Systems.

TASK: 66

TASK TITLE: Investigation of Advanced Metallic Composites II

TASK OBJECTIVE: To develop an understanding of the relationships between the chemical and thermodynamic properties of fiber/matrix interface systems, the bonding characteristics of fiber/matrix interfaces, and composite properties in advanced metallic composites.

SCIENTIST: Douglas B. Gundel, Ph.D.

DESCRIPTION OF WORK:

This project was divided into two parts. Part 1 related the findings of an experimental investigation of interface failure in single and multiple-fiber transverse tensile tests, while Part 2 was the modeling of the local stresses in the same materials. These two parts were complimentary and necessary to fully understand the fundamental aspects of interface failure under transverse loading.

Under transverse (normal to the fiber axis) tension, fiber-matrix debonding in fiber-reinforced titanium matrix composites results in reductions in specimen compliance and ultimate strength, and increased loading of the matrix. The interface structure and chemistry have a large influence on the debond stress and therefore contribute significantly to the transverse composite behavior. The

cruciform specimen geometry was employed in Part 1 over a range of specimen thicknesses to investigate the remote stress levels where debonding initiates in Ti-6Al-4V composites containing SCS-6 (C+Si coating), SCS-0 (no coating), and Trimarc 1 (C coating) SiC fibers. The different surface conditions of the fibers elicited a range of remote interface debond stresses with SCS-0 being the strongest and Trimarc 1 being the weakest. Multiple-fiber, single-ply specimens of the three different fibers revealed that the remote debond stress did not vary for SCS-6 and Trimarc 1 compared to single-fiber tests, but were slightly lower for SCS-0.

In Part 2, both analytical and numerical techniques were employed to determine the interface stresses for several geometries and interpret the applied debond loads measured for different specimen geometries with the three SiC fibers studied in Part 1. For single-fiber tests, the specimen thickness was found to have little influence over the range modeled (250-550μm). The presence of neighboring fibers was found to significantly alter the interfacial stress levels upon loading for a single-ply composite, but not for a multiple-ply arrangement, where only the residual stress level was influenced.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 72, The Transverse Tensile Behavior of SiC Fiber/Ti-6Al-4V Composites.

TASK: 67

TASK TITLE: Electrical Properties of Antimonide-Arsenide Quantum Wells

TASK OBJECTIVE: Determine the electrical properties of semiconductor quantum wells made of III-V semiconductors based on antimony and arsenic and determine the effect of barrier height and well thickness on the carrier density and mobility.

SCIENTIST: Ikai Lo, Ph.D.

DESCRIPTION OF WORK:

The electronic properties of $Al_XGa_{1-X}Sb$/InAs quantum wells were investigated by the Shubnikov-de Haas measurements for magnetic fields up to 4.5T and at a temperature about 1.2K. Two sets of samples were used for the study. One set was provided by WL/AADP grown by R. Kaspi. The other was delivered from Northwestern University by M. Razeghi. From the Shubnikov-de Haas measurements the electron density of the two-dimensional electron gas in the InAs well was determined. After illuminating the samples at low temperatures, the electron density for all samples decreased. From the amplitude of Shubnikov-de Haas oscillation, the effect of well thickness on the two-dimensional electron-hole system was evaluated and it was found that the electron in the InAs well of the sample which contains more hole carriers has a smaller quantum lifetime. For the sample with thinnest well, the interface roughness dominated the scattering mechanism but when the number of hole carriers increased by a negative persistent photoconductivity effect it became less important and finally was dominated by the electron-hole scattering. The negative persistent photoconductivity effect was used as a tool to reduce the electron density in the well and increase the hole density in the barriers.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 48, Electrical Properties of Antimonide-Arsenide Quantum Wells.

TASK: 68

TASK TITLE: Multilayer and Functionally Gradient Films for Sliding Wear

TASK OBJECTIVE: To develop new tribological films, which have multilayer and functionally gradient structures. To investigate the use of carbides, diamond-like carbon (DLC) and carbon nitride (CN) in these films. To significantly improve friction and wear characteristics of sliding pairs, particularly, in MEMS devices.

SCIENTIST: Andrey A. Voevodin, Ph.D.

DESCRIPTION OF WORK:

This research project entailed the development of advanced carbon based tribological coatings. Pulsed laser deposition (PLD) was used to produce super-hard (60-70 GPa) diamond-like carbon (DLC) with a low friction coefficient and a self-lubrication. Attention was given to the improvement of the coating toughness. A hybrid of magnetron sputtering and PLD was used to deposit coatings with architectures designed to withstand 1-10 GPa contact stress. This included: (i) composite coatings combining hydrogen-free and hydrogenated DLC; (ii) functionally gradient metal/ceramic/DLC; and (iii) nanolayered coatings with crystalline metal and carbide interlayers (about 10 nm thick) between DLC layers (about 60 nm thick). The research led to the fabrication of thin (2-3 μm) DLC-based coatings for steel substrates, which could maintain friction coefficient of about 0.1 for several million cycles of unlubricated sliding at contact pressures above 1 GPa. Their adhesion scratch resistance exceeded that of conventional ceramic (TiN, TiC) coatings.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 76, Multilayer and Functionally Gradient Films for Sliding Wear Protection.

TASK: 69

TASK TITLE: Fatigue and Fracture of Fibrous Monolithic Ceramics

TASK OBJECTIVE: To identify and document aspects of fatigue, fracture toughness, and fracture behavior in highly textured ceramics, with and without continuous fibers.

SCIENTIST: James M. Staehler, Ph.D.

DESCRIPTION OF WORK:

The research was broken down into two sections, each with its own scope and purpose. The first section looked at the oxidation behavior of $Si_3N_4$-BN fibrous monolithic ceramic using the thermogravimetric equipment. Small blocks of the material were exposed for several hours at 800, 1000, and 1150°C in air. No measurable net mass loss was observed in the specimen exposed at 800°C. In addition, this specimen showed no distinguishable change in specific surface area using

gas adsorption measurements before and after the thermogravimetric runs. A very slight mass change was observed at 1000 and 1150°C but again no appreciable change in specific surface area.

The second section examined the oxidation behavior of a Nicalon/BN/SiC/$Al_2O_3$ ceramic matrix composite. Unlike the work with the fibrous monolith, in this case the approach taken was to expose several fracture surfaces to an oxidizing environment using a tube furnace. The objective was to determine if silica readily formed at the fiber interface upon exposure to air at high temperatures. These results were then contrasted with previous results from polished specimens in order to determine if the polishing procedure used had caused earlier silica formations. Silica forms readily on the fracture surface at fiber interfaces for temperatures at and above 1000°C, indicating that the polishing procedures used in the past had not caused the formations outright.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 57, Oxidation Behavior of a Fibrous Monolithic Ceramic and a Nicalon Reinforced Ceramic Matrix Composite.

TASK: 70

TASK TITLE: Surface Chemistry Investigation of Boundary Lubrication of Perfluoropolyalkylethers

TASK OBJECTIVE: To elucidate the chemical interactions occurring between bearing materials and perfluoropolyalkylether lubricants under boundary lubrication conditions.

SCIENTIST: Jeffrey N. Cutler, Ph.D.

DESCRIPTION OF WORK:

The research provided critical insights regarding the interactions of perfluoropolyalkylether (PFPAE) additives with Fe-based alloys. PFPAEs are primary candidates for the development of high temperature liquid lubricants for the next generation of turbine engines because of their chemical and thermal stability. However, a PFPAE must be tailored for its particular application by the addition of soluble additives. Currently, two additives that show promise for improved performance are a substituted triphenyl phosphine and a bis-substituted benzothiazole. To date,

little work has been reported on the mechanism by which these additives actually improve overall performance. In order to gain some understanding of how these additives work, a series of oxidation-corrosion tests were performed using these additives in Demnum with the resulting coupons examined by X-ray Absorption Near Edge Structure (XANES) and Conversion Electron Mössbauer Spectroscopy (CEMS).

Even though both additives improved corrosion performance relative to the unformulated PFPAE fluid by forming a protective barrier, the way in which this was accomplished differs greatly. For the triphenyl phosphine additive, a surface chemical reaction occurs in which the starting additive is transformed to an iron polyphosphate glassy material. In contrast, the benzothiazole additive appeared to remain intact on the surface thereby forming a physical barrier. Below the additive surface layer, CEMS showed the formation of a mixed iron oxy-fluoride on the surface. The rate of formation of this underlayer appeared to be controlled by the film formed by the additive.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 82, X-ray Absorption Near Edge Structure (XANES) and Conversion Electron Mössbauer Spectroscopy (CEMS) Study of Perfluoropolyalkylether Based Additives.

TASK: 71

This task was canceled.

TASK: 72

TASK TITLE: Laser Hardening Materials Research & Development

TASK OBJECTIVE: Provide sensor level expertise for research and development of revolutionary materials and processes using structured polymers and liquid crystals for laser hardened optical materials.

SCIENTIST: Donald R. Wiff, Ph.D., Kent State University

DESCRIPTION OF WORK:

This task covered new research ideas for the Laser Hardened Materials Branch to consider. It was completed by someone who spent the major portion of his professional career in the Air Force Materials Directorate. Having been in an industrial laboratory for eleven years he brought a new outlook to the research emphasis, but the findings were tempered by knowing the culture and dreams of many who spent their entire lives to make the Materials Laboratory a world-class research facility. Some of the ideas brought forward may have already been initiated and were not obvious to the observer.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 50, Laser Hardened Materials Research & Development.

TASK: 73

TASK TITLE: Geometric and Electronic Properties of the Ground and Excited States of Organic Electronic and Photonic Materials.

TASK OBJECTIVE: To further understanding of the microscopic mechanisms involved in the conduction of charge and nonlinear optical response in fully conjugated conducting polymers.

SCIENTIST: Xiaofeng Duan, Ph.D.

DESCRIPTION OF WORK:

The structures and energetics as well as band gaps of poly-(1,3-thioeno-thiophene-squarine) and its dianion were calculated by means of semi-empirical Hamiltonian and ab initio quantum mechanic theories. The polymer is not stable thermodynamically because of its large electron affinity and it could have a narrow band gap as low as 0.4 ~ 0.7 eV predicted by either considering HOMO-LUMO difference at ab initio HF level or by counting the singlet-triplet state energy difference at ab initio MP2 level or by means of crystal orbital calculation at semi-empirical EHMO level. The band gap of the dianionic polymer is larger than the neutral polymer and it is about 1.0

eV ~ 1.5 eV at ab initio HF or MP2 level when the energy difference between singlet and triplet states is considered.

The NLO properties for disulfide diffuse system which has three dianions i-Mnt, cis-Mnt, trans-Mnt and one neutral molecule n-Mnt were investigated theoretically. The NLO properties of the ionic compounds of the three dianions with counter ions: $[NH_4]^+$ and $[PMe_4]^+$ were also studied. The structures of all the species were optimized at RHF/6-31G level of theory. The NLO properties were calculated at either RHF or MP2 level with basis set DH*+dp and it was found that all the dianions have larger polarizabilities than the neutral molecule. It is also true for the first and second hyperpolarizabilities. After forming the ionic complexes with counter ions, these dianions still show larger molecular weighted polarizabilities and second order hyperpolarizabilities than that of the neutral molecule.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 75, Theoretical Studies: I. Electronic Structure and Energy Band Gap Studies for Poly-(1,3-Thiophene-Squarine) and its Dianion; II. Nonlinear Properties of Disulfide Diffuse Molecular System.

TASK: 74

TASK TITLE: Characterization of Nonlinear Optical Properties using the Z-Scan Technique

TASK OBJECTIVE: To use the Z-scan techniques to investigate nonlinear optical properties. The importance of different mechanisms, including nonlinear absorption, nonlinear refraction, and other nonlinear processes, to the observed nonlinear optical signals will be studied.

SCIENTIST: David Forrai, M.S.

DESCRIPTION OF WORK:

1,3-dimethylimidazole-2-thione and related organic materials are a new class of organic nonlinear optical materials developed at the Georgia Tech Research Institute (GTRI). Early investigations of these materials at GTRI showed a large, negative third order nonlinear response

from these materials using an 80 nanosecond pulsed laser. This investigation characterized the third order nonlinear response of these materials using a 30 picosecond pulsed laser at the same wavelength. The hypothesis was that these materials would exhibit a positive change in refractive index under picosecond excitation and that the large negative responses at nanosecond excitation were due to nonlinear absorption. The results of this study showed that these materials exhibited a small amount of positive refractive index change and considerable nonlinear absorption. The positive nonlinear change in refractive index was attributed to rotation of the molecule. The nonlinear absorption was attributed to a two photon absorption followed by a reverse saturation absorption.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 66, Picosecond Nonlinear Optical Measurements of Imidazolium-Stabilized 1,2 Dipoles.

TASK: 75

TASK TITLE: Completion of Understanding Microstructure Fracture Relationships

TASK OBJECTIVE: To complete characterization and documentation of microstructure and fracture processes in metallic materials.

SCIENTIST: N.U. Deshpande

DESCRIPTION OF WORK:

In this study, quantitative microscopic and quantitative fractographic characterization of g TiAl alloy was carried out, to understand the role played by microstructural parameters and fracture modes in controlling the R-curve behavior as a function of loading rate and the grain size of the fully lamellar microstructure. It was shown that the crack growth resistance decreases, as the grain size increases, further as the loading rate increases the crack growth resistance decreases.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 54, Quantitative Microscopic and Quantitative Characterization of g Titanium-Aluminide (g-TiAl).

TASK: 76

TASK TITLE: Silicon and Carbon Solid Source Effusion Cell Evaluation

TASK OBJECTIVE: Growth of high quality homoepitaxial SiC with improved dopant characteristics, low defects, high purity, and sharp interfaces. The approach will utilize solid source MBE growth process. MBE is the technique of choice for production of most epitaxial semiconductor films - highest quality, lowest cost. It is also a superior research tool. The ultra-high vacuum environment provides the opportunity to grow the most pure materials as well as the use of in-situ sensors to follow and control the growth processes. The need for high quality SiC epitaxial films was identified by the recent SiC consortium as the very highest priority. That is, the need for epitaxial films is now.

SCIENTIST: Matthew Seaford, Multi-Layered Structures, Inc.

DESCRIPTION OF WORK:

The objective of this research was the growth of high quality homoepitaxial SiC with improved dopant characteristics, low defects, high purity, and sharp interfaces. The approach utilized solid state MBE growth process. MBE was the technique of choice for production of epitaxial semiconductor films due to higher quality and lower cost. It is also a superior research tool. The ultra-high vacuum environment provided the opportunity to grow the most pure materials as well as the use of in-situ sensors to follow and control the growth processes. The need for high quality SiC epitaxial films was identified by the recent SiC consortium as the very highest priority.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 77, Silicon and Carbon Solid Source Effusion Cell Evaluation.

TASK: 77

TASK TITLE: Compatible Data Collection for Surface Analysis Equipment

TASK OBJECTIVE: To continue to develop data collection and manipulation capabilities and implement them on existing surface analytical equipment.

SCIENTIST: Donald R. Thomas, M.S.

DESCRIPTION OF WORK:

The Surface Interactions Group of the Air Force Wright Laboratory's MLBM division operates a number of surface analysis systems. Each of these systems support one or more of the following analysis techniques:

- Auger electron spectroscopy (AES)
- X-ray photoelectron spectroscopy (XPS)
- Secondary-ion mass spectroscopy (SIMS)
- Ion-scattering spectroscopy (ISS)

This research project was an attempt to create a compatible data collection system that supports each of these techniques on each surface analysis system and will meet the following goals:

- Present a common interface across each of the surface analysis systems and across each of the analysis techniques.
- Create a modern, graphical-user interface, which is intuitive and easy to use.
- Allow exporting of data to a standard file format which can be imported into various third-party data processing software.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume Volume 56, Development of a Compatible Data Collection and Analysis System.

TASK: 78

TASK TITLE: Texture Development in Aerospace Alloys

TASK OBJECTIVE: To establish the effect of thermomechanical processing variables on macro and micro-texture development in titanium and nickel base alloys.

SCIENTIST: David P. Delo

DESCRIPTION OF WORK:

Thermo-mechanical processing induces microstructure and property changes in titanium alloys that can be controlled by applying a proper understanding of the relationships between processing, microstructure and properties. The present work combined experimental processing observations with computational simulation results to improve understanding of thermo-mechanical processes. The results of the coupled experiments and simulations will be used in the development and/or refinement of material processing models.

Ti-6Al-4V billets deformed at elevated temperatures by simple shear in a special extrusion die exhibited non-uniform flow characterized by edge cracking and flow localization leading to the eventual formation of severe shear bands. The general behavior was reproduced computationally using 2-D and 3-D finite element simulations. Die chilling and the flow softening behavior of the material were found to contribute to the non-uniform flow. Load-stroke curves measured and simulated during 900°C and 985°C extrusions were found to depend on the uniformity of the material flow through the die with localization and severe shear band formation causing a reduced load maximum. The findings will be used to refine future variations of the extrusion process leading to microstructural and textural analysis.

Ti-6Al-4V and Ti-24Al-11Nb powder consolidation processes were simulated using discrete element consolidation simulation software and the results were compared with experimental observations. Some inconsistencies in the structures of actual and simulated partially consolidated compacts were identified. Differences in experimental and actual coordination numbers and contact areas were attributed to mechanistic differences between the consolidation experiments and the simulations. Experimentally observed pore anisotropy was not systematically reproduced in the

simulations. Local density variations were found to depend on initial packing arrangements even after a large amount of consolidation. The results will be used in further explaining consolidation mechanisms and developing and refining processing models.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 98, Metallurgy and Advanced Metallic Materials: Equal Channel Angular Extrusion of Ti-6Al-4V and Discrete Element Modeling of Titanium Alloy Consolidation.

TASK: 79

TASK TITLE: Excess Carriers in InGaSb/InAs Strained Layer Superlattices

TASK OBJECTIVE: Measure electronic properties of InGaSb/InAs single and multiple quantum wells and use results to determine the source of the excess electrons that have been reported in this material.

SCIENTIST: Mohamed Ahoujja, M.S.

DESCRIPTION OF WORK:

In this project electronic transport properties of molecular beam epitaxy grown InSb on GaAs substrates were investigated, using the temperature and the variable magnetic field dependent Hall effect measurements. Several samples of different layer thicknesses of InSb were studied. The variable magnetic field Hall measurements were analyzed by using the "mobility spectrum" of Beck and Anderson. The mobility spectrum for the 2 micron layer of InSb displayed only two electron mobility peaks, one corresponding to bulk InSb and the other to the surface layer. For the 9 micron layer, the surface layer, the bulk InSb, and the GaAs/InSb interface peaks were observed in the mobility spectrum. It was observed that at room temperature the 9 micron layer changed from n-type to p-type. It may be concluded from this study that the interface contribution to the conduction depends on the InSb layer thickness.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 60, Electron Transport Characterization of Molecular Beam Epitaxy Grown InSb on GaAs Substrates

TASK: 80

TASK TITLE: Threshold Crack Growth Behavior in Titanium Alloys

TASK OBJECTIVE: To evaluate the near-threshold crack growth behavior in titanium alloys under high cycle fatigue and combined high cycle/low cycle fatigue. To develop mechanistic models for predicting near-threshold crack growth behavior in titanium alloys, and develop a method of determining "true" threshold crack growth values for titanium alloys.

SCIENTIST: Yuri N. Lenets, Ph.D.

DESCRIPTION OF WORK:

In real components operating under high R-ratios, the crack propagation usually commences in the presence of large cyclic plastic zones. Such a situation can be adequately represented by the fatigue crack growth threshold test with an abrupt load change while keeping constant R or $K_{ma}$. However, no attempt has been made so far to evaluate experimentally the load history effects on the fatigue crack growth threshold values furnished by such threshold test method.

In the present study, fatigue crack growth thresholds for the IMI 834 Ti-alloy were determined at three different values of $K_{max}$ equal to 6, 10 and 25 MPa$\sqrt{m}$, using two different load patterns, both including an abrupt change in the $\Delta K$ value at constant $K_{max}$. Fractographic examination revealed relatively brittle FCG mechanism (quasi-cleavage) of predominantly transgranular character being representative for all loading regimes used in the present study. Increasing $\Delta K$ applied to the initially dormant crack resulted in higher FCG thresholds as compared to the situation when decreasing $\Delta K$ values were applied to the growing crack. The discrepancy can be attributed to the crack tip shielding associated with residual stresses in front of the fatigue crack rather than with fracture surface contact behind the crack tip.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 83, Threshold Crack Growth Behavior in Titanium Alloys: Effect of Cyclic Load History.

TASK: 81

TASK TITLE: Investigation of Advanced Metallic Composites III

TASK OBJECTIVE: To develop an understanding of the relationships between the composition and microstructure of matrices, the size and distribution of reinforcement, the character of the particle/matrix interface, and composite properties in advanced metallic composites.

SCIENTIST: Awadh B. Pandey, Ph.D.

DESCRIPTION OF WORK:

Experiments were performed on a powder metallurgically processed at15 volume percent 7093/SiC discontinuously reinforced aluminum (DRA) matrix composite in different heat treatment conditions in order to probe the influence of the matrix microstructure and its deformation and failure characteristics on the composite response. The elongation varied inversely as the strength, similar to monolithic Al-alloys, which indicates that the matrix rupture conditions play a key role in shaping the composite properties. Damage in tensile compounds were quantified using metallographic and replication techniques. Those measurements revealed that in most heat treatment conditions, damage was present as particle cracks and interface debonds, with peak aged material exhibiting a high localization of damage and plasticity. The mirror halves of fracture surfaces showed that for the same microstructures there was a dominance of particle cracks, suggesting that this mode took dominance under constrained deformation conditions during crack propagation. When the composite strength became less than 400 MPa, then near-interface matrix rupture became dominant compared to particle cracking. When the composite strength became less than 400 MPa, then near-interface matrix rupture became dominant compared to particle cracking. Fracture toughness tests show that it is important to maintain proper geometry and testing procedures to obtain valid fracture toughness data. Over aged microstructures did reveal recovery of fracture toughness on aging past the peak aged conditions. Thus the overall behavior was a

monotonic decrease of toughness with strength, paralleling the elongation trend. Damage and fracture micromechanisms responsible for the observed data were investigated, and modeling for the strength, elongation, toughness, and damage were also performed.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 87, Experiments and Analyses of Deformation and Fracture of Particle-Reinforced Aluminum Alloy Composites.

TASK: 82

TASK TITLE: Fracture Characterization of Cross-Ply Ceramic Matrix Composites

TASK OBJECTIVE: To characterize the fracture characteristics of cross-ply ceramic matrix composites using pure mode I, pure mode II, and a range of mixed mode loading.

SCIENTIST: Tor W. Sherwood, B.S.

DESCRIPTION OF WORK:

A technique for investigating the mixed mode fracture toughness of a ceramic matrix composite as a function of lay-up and temperature was described. A relatively new test technique, termed the Single Leg Bending (SLB) test, was used to determine the mixed mode strain energy release rate. A compliance calibration technique for data reduction was utilized.

Ceramic matrix composite specimens with a cross-ply, $[(90/0)_4]_S$, lay-up were investigated and their results were compared to previous unidirectional work done by Polaha (Polaha, 1995). Two types of specimens were considered: specimens with a unidirectional fiber orientation and specimens with a $[(90/0)_4]_S$ lay-up. The effects of temperature were determined by conducting tests at room temperature and at 500°C. A laser interferometric displacement gage was utilized to detect crack advance.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 58, An Approach to Characterizing the Mixed

Mode Fracture Toughness of a Ceramic Matrix Composite as a Function of Lay-up and Temperature

TASK: 83

TASK TITLE: Fracture Characterization of Unidirectional Ceramic Matrix Composites

TASK OBJECTIVE: To characterize the fracture characteristics of unidirectional ceramic matrix composites using pure mode I, pure mode II, and a range of mixed mode loading.

SCIENTIST: Jonathan J. Polaha, B.S.

DESCRIPTION OF WORK:

This project investigated the effect of mode ratio and elevated temperature on the fracture toughness of a unidirectional ceramic matrix composite. Different mode ratios were considered at both room and elevated temperature; pure mode I, pure mode II, and a mixed-mode condition. The Double Cantilever Beam test and End-notched Flexure test were used to determine the critical strain energy release rates for mode I and mode II loading, respectively. A relatively new test, the Single-Leg Bending test, was used to determine the critical strain energy release rate for the mixed-mode condition. A compliance calibration method was used for the data reduction of all three test types. The load versus displacement data from both a laser interferometric displacement gage and an LVDT were examined during each test to detect the initiation of fracture.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 47, An Approach for Characterizing the Fracture Toughness of a Ceramic Matrix Composite as a Function of Mode Ratio.

TASK: 84

TASK TITLE: Characterization of Wide Area Corrosion Damage

TASK OBJECTIVE: To provide a methodology for the characterization of corrosion damage in thin section aircraft structures.

SCIENTIST: William Mullins, Ph.D., Technical Management Concepts, Inc.

DESCRIPTION OF WORK:

A simple kinetic model for general attack has been proposed. This model predicts the evolution of a rough surface with a Hausdorff (fractal) dimension that approaches 2.5 as a limiting case. The model predicts a measurable critical length scale that can be used to determine the time of exposure. A simple kinetic model for exfoliation has also been proposed. The model predicts the evolution of surface profiles similar to those of general attack. Intergranular penetration was shown to be not directly related to surface morphology, and formed wide-sense stationary "White-noise" interface. Experimental results were shown for 2024-T3 which corroborate the models for the limiting case. Finally, simple models for surface stress concentration factors were developed which relate the surface stress concentration factor distribution to the surface morphology.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 91, Stochastic Kinetics Corrosion and Implications of Surface Properties.

TASK: 85

TASK TITLE: Smart Materials and Structures

TASK OBJECTIVE: The primary focus will be directed to research efforts and issues related to mechanics and mechanical behavior of smart materials and structures, such as durability, failure modes, fracture and damage mechanisms, constitutive behavior under combined mechanical, thermal and electrical loadings (especially nonlinear response), host and sensor/actuator interface issues.

SCIENTIST: Diann Erbschloe Brei, Ph.D.

DESCRIPTION OF WORK:

The objectives of this task were to develop an overview of the Smart Materials and Structures field, identify potential Air Force applications and pay-offs, and list critical fundamental research issues that need to be addressed. Seven key technologies for smart structures were addressed with examples of current research in each. Several Air Force applications, where these seven technologies may be applied, were listed along with the potential pay-offs for Aerospace Structures, Armament and Uninhabited Systems and Space Systems. Unfortunately, there is still considerable research into basic issues that must be conducted before these applications and pay-offs can be realized. The basic research issues range from specific ones for the components that makeup the smart structure such as sensors, actuators, and power electronics to more widespread ones that affect all aspects of the smart structures such as integrity, integration, and modeling/characterization. An additional goal during the course of this task was to initiate a research program in one of the critical basic research areas. Integrity of smart structures was found to be the most critical issue that must be overcome before smart structures can be used for Air Force applications. A more detailed investigation into this research area was conducted and recommendations for a three year research program were given.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 51, Smart Structures.

TASK: 86

This task was canceled.

TASK: 87

TASK TITLE: Deposition and Atomic Force Microscope (AFM) Characterization of Solid Lubricants and Hard Materials

TASK OBJECTIVE: To conduct research on the growth and characterization of solid lubricants and hard materials that provide low friction surfaces and/or wear protection. To design, assemble, and operate vacuum deposition equipment and an AFM. To develop standard and AFM-based tribological tests to determine

mechanical and friction/wear properties of materials on an atomic level as part of the overall research and development program in advanced tribological materials.

SCIENTIST: Josekutty Nainaparampil, Ph.D.

DESCRIPTION OF WORK:

Single crystal zinc oxide crystal and polycrystalline zinc oxide film have been analyzed by atomic force microscope, a single asperity system. Single crystal zinc oxide (0001) face was polished to a few angstroms units roughness and scanned for topographical and lateral force contrast. Since the polished faces remain stressed from mechanical rubbing, crystals were allowed to recrystallize under annealing temperatures of 750°C - 900°C to release the stress. Upon annealing the crystal formed step like structures on its surface. Polycrystalline zinc oxide films deposited on steel as well as single crystal silicon substrates have been characterized for tribological properties. Surfaces of as deposited films and wear track formed by pin on disk type tribometer were also included for study. The topography became smoothed in wear tracks and protruding structures on the smoothed track appeared like newly formed material from tribochemical reactions. XPS could not find any ball material on these tracks. Further magnification showed grains formed in tracks and a lateral force contrast on these grains. Adhesion force variation on the steps formed on single crystal zinc oxide was also measured.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 89, Atomic and Friction Force Microscope-based Analysis of Single Crystal Zinc Oxide and Polycrystalline Zinc Oxide Thin Films.

TASK: 88

TASK TITLE: Deep Levels in Silicon Carbide

TASK OBJECTIVE: Determine the effect of polytype on the deep levels present in bulk grown and epitaxial silicon carbide and evaluate possible dopants for the formation of semi-insulating SiC.

SCIENTIST: Andrew O. Evwaraye, Ph.D.

DESCRIPTION OF WORK:

Bulk and epitaxial layers silicon carbide of 6h- and 4h- polytypes were studied using capacitance-voltage measurements, thermal admittance spectroscopy, optical admittance spectroscopy and high temperature Hall effect measurements. The indirect gap of SiC, while ruling out efficient lasing, does not preclude optical transition altogether. However, these transitions can take place only with the assistance of phonons. Phonon emission and absorption lines appeared in Optical Admittance Spectra of SiC between 300 nm to 500 nm. The strongest absorption was seen for the transverse acoustic phonon assisted transition from the top of the valence band to the second conduction band minimum. It is well known that boron substitutes for silicon in the silicon carbide lattice occupying three inequivalent sites. The ground state energies of $E_V$ + 0.27 eV, $E_V$ + 0.31 eV, and $E_V$ + 0.38 eV were determined for the shallow boron acceptor in 6H-SiC. Consequently, the free carrier concentration does not appear to be the only determining factor for which the boron acceptor level is observed.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 88, Electrical and Optical Characterization of Silicon Carbide.

TASK: 89

TASK TITLE: Fracture Characterization of Unidirectional Ceramic Matrix Composites

TASK OBJECTIVE: To characterize the fracture characteristics of unidirectional ceramic matrix composites using pure mode I, pure mode II, and a range of mixed mode loading.

SCIENTIST: Jonathan J. Polaha, B.S.

DESCRIPTION OF WORK:

This project investigated the effect of mode ratio and elevated temperature on the fracture toughness of a unidirectional ceramic matrix composite. Specimens were implanted midplane delaminations using a mode I wedge loading technique. Different mode ratios were then considered at both room and elevated temperature; pure mode I, pure mode II, and a mixed-mode condition. The Double Cantilever Beam test and the End-notched Flexure test were used to determine the critical strain energy release rates for mode I and mode II loading, respectively. A relatively new test, the Single-Leg Bending test, was used to determine the critical strain energy release rate for the mixed-mode condition. A compliance calibration method was used for the data reduction of all three test types. The load versus displacement data from both a laser interferometric displacement gage and an LVDT was examined during each fracture test to detect the initiation of fracture. Fracture toughness values were presented for all mode ratios and a comparison was made between the initial mode I and test mode precrack toughnesses.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 63, An Approach for Characterizing the Fracture Toughness of a Ceramic Matrix Composite as a Function of Mode Ratio

TASK: 90

TASK TITLE: Fatigue, Fracture, and Crack Growth of Fibrous Monolithic Ceramics

TASK OBJECTIVE: To identify and document aspects of fatigue, fracture toughness, crack growth, and fracture behavior in highly textured ceramics, with and without continuous fibers.

SCIENTIST: James M. Staehler, Ph.D.

DESCRIPTION OF WORK:

The objective of this research was to obtain an understanding of the mechanical behavior of fibrous monolithic ceramics under tensile loading conditions at room and elevated temperatures. Three different fibrous monolithic ceramic material systems were examined. They included two diborides; HfB2/BN and ZrB2/BN, plus a third non-boride material, Si3N4/BN. A number of

different architectures were considered as well, which included unidirectional, 0-90° cross-plies, and quasi-isotropic, although not all were considered within each of the three material systems. Material manufactured from multi-filament coextrusions for contrasted with material from single filament extrusions for the diboride formulations. Mechanical characterization included: tensile fast fracture at room and 1150°C, tensile creep rupture at 1000°C (Si3N4/BN only) and 1150°C, and tension-tension fatigue at 1000°C (Si3N4/BN only) and 1150°C. Sample populations were small due to the shortage of test material. However, data shows the Si3N4/BN to have the best oxidation resistance at 1150°C but that it is still susceptible to strain accumulations under sustained and cyclic loading conditions. Both diboride materials suffered from clear oxidation at 1150°C but neither appeared to strain measurably. The unidirectional Si3N4/BN had by far the best ultimate tensile strengths, but there was little advantage in strength between the three material systems for the cross-ply architecture. For the diborides, the multi-filament and single filament unidirectional materials had similar mechanical properties.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 102, Mechanical Behavior and Life Predictions of Three Fibrous Monolithic Ceramics.

TASK: 91

TASK TITLE: Creep Rupture of BlackGlas Composites

TASK OBJECTIVE: To identify and document aspects of creep behavior and environmental degradation during creep rupture testing of Nicalon/BlackGlas ceramic matrix composites.

SCIENTIST: Shin S. Lee, Ph.D.

DESCRIPTION OF WORK:

Applying high-temperature CMCs is critical in advancing aerospace technology. Currently, both the B-2 Bomber and the F-117 Stealth Fighter are experiencing very high maintenance on all the exhaust washed structures. Blackglas™ CMCs are actively being considered for replacing current Bill-of-Materials. In order to get this activity underway, the long-term performance and

durability of Blackglas CMCs was examined. Results indicated that Blackglas CMCs exhibit good mechanical performance at low applied stress and temperatures below 600°C.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 73, Long-Term Performance and Durability of Blackglas™ CMCs.

TASK: 92

TASK TITLE: Nanocrystalline Oxides for Lubrication in Extreme Environments

TASK OBJECTIVE: Development of nanocrystalline oxide solid lubricant materials useful to 850°C.

SCIENTIST: Somuri V. Prasad, Ph.D.

DESCRIPTION OF WORK:

The objective of this research was the characterization of pulsed laser deposited zinc oxide films. Four different permutations of substrate temperature and oxygen partial pressure (RT/V, RT/$O_2$, 300°C/V and 300°C/$O_2$) were employed to grow films with different microstructures and stoichiometry. Films were characterized by Raman spectroscopy, x-ray diffraction and transmission electron microscopy. Results showed that all the films were crystalline with a hexagonal crystal structure. The RT/V films were highly textured; the other films had a combination of texture and randomly oriented grains. Raman spectroscopy revealed significant differences among the four sets of films; Raman spectrum of 300C/$O_2$ film closely resembled that of the target material. A schematic depiction of the microstructure, comprising of nanocolumns and randomly oriented nanocrystalline grains, for generating lubricious oxides was presented in the final report.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 78, Characterization of Pulsed Laser Deposited Zinc Oxide Films.

TASK: 93

TASK TITLE: Microstructural Characterization of Strain and Strain-Rate Effects During Hot Working of g-TiAl

TASK OBJECTIVE: To determine dynamical effects during hot working for the objective of developing mathematical models.

SCIENTIST: N.U. Deshpande, Ph.D.

DESCRIPTION OF WORK:

The main objective of this work was to apply quantitative microscopic techniques to: (1) understand the influence of strain rate sequence on the final microstructure of the fully lamellar γ Ti-49Al-2V alloy, and (2) characterize the microstructural properties of a plain carbon steel, which was hot extruded using a conical die.

Quantitative Microscopic characterization of effect of strain rate sequence on the final microstructure of the fully lamellar γ Ti-49Al-2V alloy has shown that the final microstructure is strain rate sequence dependent. Quantitative microscopic analysis of hot extruded, plain carbon steel, using conical die, has shown that the microstructural parameters like size of the pearlite and the volume fraction of the ferrite are location dependent. In the central conical portion of the extrudate the pearlite grain size decreases in a stepwise manner.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 65, Quantitative Microscopic Study On: (1) Influence of Strain Rate Sequence on Microstructure of γ Ti-49Al-2V & (2) Development of Microstructural Profile in a Hot Extruded Steel.

TASK: 94

TASK TITLE: Compatible Data Collection for Surface Analysis Equipment

TASK OBJECTIVE: To continue to develop data collection and manipulation capabilities and implement them on existing surface analytical equipment.

SCIENTIST: Donald R. Thomas, Ph.D., propellerHead, Inc.

DESCRIPTION OF WORK:

The Surface Interactions Group of the Air Force Wright Laboratory's MLBM division operates a number of surface analysis systems. Each of these systems support one or more of the following analysis techniques:

- Auger electron spectroscopy (AES)
- X-ray photoelectron spectroscopy (XPS)
- Secondary-ion mass spectroscopy (SIMS)
- Ion-scattering spectroscopy (ISS)

This research project was an attempt to create a compatible data collection system which would support each of these techniques on each surface analysis system and would meet the following goals:

- Present a common interface across each of the surface analysis systems and cross each of the analysis techniques.
- Create a modern, graphical-user interface, which would be intuitive and easy to use.
- Allow exporting of data to a standard file format which could be imported into various third-party data processing software.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 93, Development of a Compatible Data Collection and Analysis System.

TASK: 95

TASK TITLE: Rapid Solidification Processing of Sheet and Laminate Materials

TASK OBJECTIVE: To establish the relationship between processing variables, microstructure, and properties of rapidly solidified sheet and multilayer laminates.

SCIENTIST: Amit K. Ghosh, Ph.D.

DESCRIPTION OF WORK:

Prediction of processing induced internal damage in materials is an important requirement toward understanding their limitations in service. This report summarizes a combination of experimental and analytical research performed to identify and understand the sources of cavitation during hot forming and superplastic forming of aerospace structural materials, and provide a quantitative estimate of the initial growth of the cavities. The report is presented in three sections, each being a self contained research paper in itself. The first two sections deal with the cavitation issue. Cavitation at elevated temperature is a grain boundary phenomenon, as the boundaries weaken to allow sliding between the grains above the equicohesive temperature (> ~500°C for Ti-6Al-4V, and ~290°C for Aluminum alloys). Prior models suggested that grain boundary voids grow initially by diffusion, but the rates are too slow to be realistic. It has been shown in the first section of the report that overcoming of interface surface tension is not a critical requirement for void growth as previously postulated. Interfaces with significant incompatibility, however, produce large enough strain concentration to debond the interface. The number of debonded sites become maximum at an intermediate temperature where unaccommodated grain boundary sliding is a maximum. Debonding has been modeled as a plastic strain-controlled phenomenon at weak interfaces but constrained by the stronger phase. This approach has been used in the second section to predict the rapid initial growth of voids.

The third section of the report has considered the deformation behavior of two-phase model laminate materials to understand the orientation dependence of strength and strain hardening behavior. Eventually, the individual orientation models need to be combined to predict the overall deformation behavior of a polycrystalline laminate material, e.g., forging of lamellar TiAl alloys.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 182, Analysis of Cavitation Damage during High Temperature Processing and Laminate Anisotropy.

TASK: 96

TASK TITLE: Organic Coating Technology

TASK OBJECTIVE: Formulation of organic coatings with the state-of-the-art commercially available raw materials. These coatings will be the bases for a fundamental study on mechanisms and degradation.

SCIENTIST: A. Gloria W. Kalman, M.S.

DESCRIPTION OF WORK:

The main objective of this work was to formulate coatings that will be used to explore degradation mechanisms in aircraft coatings, and obtain a fundamental understanding of what polymer system would lead to a permanent foundation layer or primer of thirty years service life and an eight years durable topcoat.

New primer systems were formulated with covalent bonding to aluminum substrate and tests were performed to demonstrate superior adhesion performance of sol gel/new primer system vs standard currently used paint system. Also attempts to formulate new topcoat systems for Durable/Cleanable Air Force effort were completed.

Preliminary results showed that the new coating systems have good adhesion to aluminum, probably due to covalent bonding from substrate to primer through the adequate sol gel coating: epoxy and acrylate. The new UV cured epoxy system was at least equivalent to the standard as for hydrolytic stability. Further studies at specified dry film thicknesses, and statistical results are needed. Auger, XPS, Electrochemical tests were ongoing and could give more data for conclusions. As for topcoats new experimental water based polymers from Bayer could be a good backbone starting point for the Durable/Cleanable Topcoat Program.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 90, Organic Coating Technology.

TASK: 97

TASK TITLE: Deformation Mechanisms in Gamma Titanium Aluminides

TASK OBJECTIVE: To analyze, characterize, and understand the fundamental deformation behavior in gamma titanium aluminides.

SCIENTIST: Sriram Seshagiri, Ph.D.

DESCRIPTION OF WORK:

This project consisted of two parts: Part I was entitled "Deformation Substructure Evolution Pertaining to 1/2<110] Unit Dislocations in TiAl Alloys", and Part II was entitled "Hall-Petch Correlation Studies in Fully-Lamellar TiAl Alloys".

In Part I, it was shown that in single-phase, coarse grained TiAl, at room temperature (RT) and above, much of the plastic strain was carried by jogged 1/2<110] unit dislocations. Observations in this paper suggest that in ($\alpha_2+\gamma$) lamellar TiAl the same mechanisms would operate within $\gamma$ lamellae, but now dislocations must overcome both point (jog) obstacles and planar (lamellar boundary) obstacles. There was some evidence that the two obstacles could be linked, that cross-slip was shown to be more frequent in thinner lamellae. This was consistent with the observation that in the thinnest lamellae, deformation was mostly carried by twins instead of by 1/2<110] unit dislocations.

Part II highlights important microstructural variables that give rise to Hall-Petch type strengthening behavior in polycrystalline fully-lamellar multicomponent TiAl alloys. The microstructural parameters studied included: grain size (D), thickness of the $\alpha 2$ (A) and $\gamma$ (G) lamellae, the spacing between the $\alpha 2$ lamellae (S) and the characteristic spacing ($\lambda$) between them, and $\alpha 2$ volume fraction (f). A strong HP correlation was observed between yield strength and $\lambda$, whereas such a correlation was almost negligible or absent between the grain size, and $\alpha 2$ volume

fraction. However, the $\lambda$ vs. yield strength gave a small value for the HP slope, in the range of 0.11-0.12 MPa$\sqrt{m}$, which was lower than both theoretical predictions and earlier reported measurements of 0.4-0.5 MPa$\sqrt{m}$. Recent theoretical prediction is that the yield strength in these alloys was not controlled by the mean value of $\lambda$, but rather by the thicker lamellae. Experimental validation of this prediction would be the subject of future study.

The detailed project description, methods, results, and discussion are reported in Contributive Research and Development Final Report, Volume 97, Deformation Behavior and Dislocation Mechanisms in TiAl Alloys.

TASK: 98

TASK TITLE: Project Management/Administration

TASK OBJECTIVE: To provide for those project activities necessary to establish project task orders and overall contract management and administration.

SCIENTIST: Nagu Nagarajan

DESCRIPTION OF WORK:

The contributive research and development project required extensive management and administration activities that were not readily charged to a specific task. These activities fell into three general categories:

1. Those contract management administrative requirements to establish planning and control procedures that applied to the project as a whole. Examples are status reporting, project management meetings, and other general overall project reporting.

2. Those management activities required to establish each of the task assignments. These activities could not be charged to the task since the task was not yet approved during this phase.

3. Recording and reporting the performance and cost for the overall management and administrative activities.

This task provided project management/administration from 16 December 1996 through 15 December 1997.

TASK: 99

TASK TITLE: Theoretical Study of Heterointerface Formation During Molecular Beam Epitaxy of III-V Materials

TASK OBJECTIVE: Develop computer models for heterointerface formation during MBE growth of III-V materials. Use these models to find the optimal MBE growth conditions for atomically abrupt interfaces.

SCIENTIST: Krishnamurthy Mahalingam, Ph.D.

DESCRIPTION OF WORK:

A comprehensive, quantitatively accurate Monte Carlo model for AlGaAs/GaAs (001) molecular beam epitaxy was developed. This model was applied within the solid-on-solid approximation, explicitly accounting for deposition, surface diffusion and deposition of both the group-III and group-V species. The parameters for the model were determined by matching model results to Ga desorption data measured by desorption mass spectroscopy. The model accurately reproduced transients in the Ga desorption signal during formation of the AlGaAs-on-GaAs heterointerface and also predicted the stoichiometry profile near the interface. Furthermore, the model revealed that Al-Ga surface exchange mechanism and changes in V/III flux ratio during opening and closing of the Al shutter had a significant effect on compositional abruptness of the AlGaAs-on-GaAs heterointerface. It was shown that high-resolution transmission electron microscopy employing the chemical lattice imaging technique was well suited to verify the predictions of the model. Details on the sample preparation procedures and precautions to be taken when employing a field-emission transmission electron microscope to perform chemical lattice imaging have also been presented.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development, Volume 105, Stoichiometry of Interfaces in AlGaAs/GaAs Heterostructures Grown by Molecular Beam Epitaxy.

TASK: 100

TASK TITLE: Reaction Kinetics of Halon and Halon Replacements

TASK OBJECTIVE: To develop a fundamental understanding of the chemical mechanisms of Halon fire suppressant action through computational chemistry. To use this understanding to evaluate alternative compounds presently being considered, and other completely different compounds, for fire suppressant capability.

SCIENTIST: Rajiv J. Berry, Ph.D.

DESCRIPTION OF WORK:

Gaussian-2 theory was utilized to compute the singlet and triplet potential energy surface (PES) for the reaction O with $CH_3CH_2I$. Species such as $CH_3CH_2IO$, $CH_3CH_2OI$, $CH_3CH_2IOH$, $CH_3CH(OH)I$ as well as the transition states that connect them were characterized. Low barrier paths leading to enhanced production of IO and OH, via the singlet adduct $CH_3CH_2IO$, were investigated. By contrast to the PES for O + $CH_3I$, HOI production via addition/dissociation through a five membered ring transition state was computed as the major pathway for O + $CH_3CH_2I$. The results provide a consistent set of thermochemical data for use in atmospheric and combustion modeling of alkyl iodides.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 95, An *Ab Initio* Study of the Reaction of Oxygen Atom with Ethyl Iodide.

TASK: 101

TASK TITLE: Infrared Nonlinear Optical Materials Research

TASK OBJECTIVE: Materials characterization, device development, and system integration of infrared optical power limiters.

SCIENTIST: Shekhar Guha, Ph.D., Optical Systems and Devices

DESCRIPTION OF WORK:

The objective of this research was to characterize infrared optical materials and develop infrared optical power limiter devices for their eventual integration into optical systems. In 1997, characterization of the optical properties of materials continued using an in-house capability developed at Wright Laboratory (WL/MLPJ) in 1996. Several novel materials were characterized in detail and their usefulness for infrared optical power limiting was demonstrated. Two new characterization facilities were set up, one for the measurement of laser-induced-damage-thresholds of nonlinear optical materials, and one for the measurement of the electro-optic coefficients of materials.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 96, Infrared Optical Power Limiter Research.

TASK: 102

This task was canceled.

TASK: 103

This task was not issued.

TASK: 104

TASK TITLE: Quantitative Microscopic Study of Effect of Deformation Path on Microstructural Evolution

TASK OBJECTIVE: To quantify the microstructural properties of γ-TiAl alloy subjected to different deformation rate conditions.

SCIENTIST: N.U. Deshpande, PhD.

DESCRIPTION OF WORK:

Effect of strain rate sequence on the final microstructure of fully lamellar γ-Ti-49Al-2V alloy was characterized using quantitative microscopy. It was observed that strain rate sequence does control the final microstructure of the alloy.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 71, Quantitative Microscopic Study of Effect of Strain Rate Sequence on the Microstructure of γ-Ti-49Al-2V Alloy.

TASK: 105

TASK TITLE: Process Model Development for use with Discrete Event System Techniques

TASK OBJECTIVE: To significantly improve manufacturing processes with respect to product quality (material properties and reproducibility/robustness of the process), manufacturing costs (fewer processing steps are usually cheaper), and delivery time (improved response to customers schedule). The overall research objective is to establish a systematic methodology for accurately modeling and significantly improving manufacturing systems and their subsystems.

SCIENTIST: Jay Gunasekera, Ph.D. , STI, Inc., Vipul Ranatunga, B.Sc., STI, Inc., and Zhizhong Zhou, Ph.D., Ohio University

DESCRIPTION OF WORK:

This research was aimed at basic research for significantly improving manufacturing processes with respect to product quality (material property and reproducibility/robustness of the process), manufacturing costs (fewer processing steps are usually cheaper), and delivery time (improved response to customers schedule). The overall research objective was to establish a systematic methodology for accurately modeling and significantly improving manufacturing systems and their sub systems.

Residual stress was, and continues to be, a significant problem in the manufacturing of forged aircraft engine disks. The simplified model has been developed to predict the residual stresses in a forged disk due to the thermal gradients.

Two basic factors have been addressed in the newly furnished casting model; riser design and the calculation of total solidification time.

The heat transfer model has been developed to predict the temperature changes in the part during the forging process. The model has been designed to handle a disk with any number of rings and the temperature predictions have been accurate within 10% as compared to FEM.

OU-Model has been developed as an enhanced slab method that relies on fundamental equations and assumptions about geometry and mechanical property variations throughout the work-piece. The work of this study has been incorporated in an existing microstructure model with OU-Model, and provides a general sub-routine which can perform high-speed computations.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 110, Process Model Development for Use with Discrete Event Systems Techniques: Residual Stress and Microstructure Predictions and Incorporation into Simplified Models.

TASK: 106

This task was canceled.

TASK: 107

TASK TITLE: Intrinsically Survivable Polymer Matrix Composites

TASK OBJECTIVE: To achieve a greater understanding of intrinsic damage tolerance mechanisms exhibited by polymers and polymer matrix composites. The research activities will explore molecular, nano-scale, and macroscopic origins of energy absorption and damage mitigation mechanisms.

SCIENTIST: Janis M. Brown, Ph.D., J.M. Brown, Inc.

DESCRIPTION OF WORK:

Traditionally, toughening of a thermosetting resin is achieved with a second phase such as rubber or thermoplastic (with micron-scale morphology). This task effort focused on exploring the structure/property/morphology relationships of nanoparticles as tougheners in organic resins. A series of nanocomposites with 0-30 wt. % montmorillonite were prepared in a DGEBA epoxy cured with polyoxypropyldiamines. Depending on the organic modifiers, exfoliated, intercalated, or immiscible nanocomposite were produced. Novel processing techniques produced transparent castings up to 20 wt. % exfoliated silicate. The influence of layered silicate distribution on mechanical relaxation and fracture properties were examined using DMA, compact tension, and microscopy. Fracture behavior of these systems varied significantly with layered silicate distribution, concentration, and reactivity. This behavior indicates that nano-reinforcement may be a viable toughening approach for high performance composite systems.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 128, Intrinsically Survivable Composites Using a Nanocomposite Approach.

TASK: 108

TASK TITLE: Solid State Nuclear Magnetic Resonance Spectroscopy of Polymeric Materials

TASK OBJECTIVE: Expand the understanding of network formation and degradation processes in high performance polymers and advanced polymer matrix composites. The goal is to understand the intrinsic mechanisms of environmental performance of these polymeric systems and develop the capability for lifetime performance prediction based on that fundamental understanding.

SCIENTIST: Brett A. Cowans, Ph.D.

DESCRIPTION OF WORK:

This research focused on two main issues. One focus was been to investigate the molecular dynamics of a proprietary polymer system using solid state $^2H$ NMR techniques. A deuterium-labeled polymer and monomer were examined to determine the amount of deuterium incorporation in the sample. Approximately two to three percent of the sites which were supposed to have a deuterium atom contained a proton instead. This amount of substitution would normally be observed unless extreme measures were taken. The preliminary $^2H$ wideline variable temperature experiments showed that at room temperature, the phenyl substituent was essentially immobile or rigid. Furthermore, there was little or no change observed when the temperature was increased to 100 C. This observation was in sharp contrast to the phenyl ring dynamics observed in polymers such as poly(carbonate) or poly(sulfone).

The second major focus has involved the installation and calibration of a spectrometer which was based on a Tecmag Libra system. This spectrometer replaces an aging Varian XL spectrometer. The installation and calibration have been discussed. Several problems with the spectrometer hardware have been discussed as well as the procedures used for repair. Recommendations have also been made for routine calibration and operation.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 101, Solid State Nuclear Magnetic Resonance Spectroscopy of Polymeric Materials.

TASK: 109

TASK TITLE: High Performance Polymers

TASK OBJECTIVE: Synthesis of high performance polymers tailored for NLO and electronic applications.

SCIENTIST: Narayanan Venkatasubramanian, Ph.D.

DESCRIPTION OF WORK:

A novel approach to processing solvent cast aromatic heterocyclic rigid-rod thermoplastic as well as thermoset molecular composites above $C_{cr}$ of the rigid-rod polymer in solution, without phase separation, has been demonstrated. Homogeneity and miscibility in the rod-matrix host blends were accomplished via acid-base interaction-mediated compatibilization between the rod and the matrix components. The composites were solvent cast by the mechanism of ionic interchange between a sulfonic acid-pendent poly(p-phenylenebenzobisimidazole), solubilized in alcohol as its triethylammonium salt and basic thermoplastics such as poly(vinylpyridine)s or secondary or tertiary amines with thermosettable phenylethynyl, nadimide and bisbenzoxazine functionalities. Morphological characterization, utilizing SEM and SAXS of as cast as well as annealed/thermally cured optically clear film composites of a broad range of compositions revealed homogeneous microstructures with no observable phase-separated domains in the 15Å-300Å scale, which indicated high miscibility, attributable to the favorable negative enthalpy of the ionic association between the rod-matrix components. A study of the thermal properties of compression molded thermoplastic rigid-rod blends with relatively low rod content showed a significant enhancement in the $T_g$ of the matrix as a function of the rod polymer incorporation in the composite. Dynamic mechanical analysis also revealed that the intimate dispersion of the rod in the thermoplastic matrix leads to noticeable increase in the storage modulus of the composite.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 106, Solvent Cast Thermoplastic and Thermoset Rigid-Rod Molecular Composites.

TASK: 110

TASK TITLE: Nondestructive Characterization of Mechanically Damaged Aircraft Titanium and Superalloy

TASK OBJECTIVE: To develop the nondestructive evaluation techniques necessary to examine mechanically worked samples for the presence of low-level damage. Additionally, current techniques will be upgraded to allow better measurement performance.

SCIENTIST: Peter B. Nagy, Ph.D.

DESCRIPTION OF WORK:

The main goal of this effort was to investigate the adverse effect of electrical grain noise on fatigue crack detectability in titanium alloys. In a manner similar to previous efforts to reduce grain noise in ultrasonic inspection of polycrystalline materials, the focus was to develop general counter strategies and specific counter measures to reduce the electrical grain noise in eddy current inspection in order to maintain good detectability in coarse grained materials and materials with large colonies containing plates of preferentially oriented much finer grains. In addition, the focus was also to exploit the electrical grain noise in titanium alloys to develop special nondestructive materials characterization techniques to evaluate the microstructure. The main achievements of this effort have been experimentally demonstrated in very strong electrical grain noise reduction in titanium alloys and theoretically explained the physical mechanism responsible for this contrast. Although the electrical anisotropy of noncubic crystals is a well known physical fact, to the best of our knowledge, the significant role played by this microscopic electrical anisotropy of individual grains in the macroscopic eddy current response of the polycrystalline material has never been pointed out or investigated in any depth.

It was found that electric anisotropy exhibited by noncubic crystallographic classes of materials can play a very similar role in electromagnetic materials characterization of polycrystalline metals to that of elastic anisotropy in ultrasonic materials characterization. Titanium is one of the few structural metals of practical importance, especially in aerospace applications, which preferentially crystallizes in hexagonal symmetry and therefore exhibits strong electrical anisotropy. There are two areas where this electrical anisotropy becomes very relevant from the point of view of fatigue. First, eddy current inspection is probably the most commonly used nondestructive testing technique for fatigue crack detection in airframe structures and engine components. Electrical grain noise presents the same problem in eddy current crack detection as acoustic grain noise does in ultrasonic flaw detection. Second, proper microstructure is absolutely essential for assuring good fatigue tolerance in the material and the electrical grain noise can be exploited for nondestructive characterization of the microstructure by eddy current inspection in the same way as acoustic grain noise is used in ultrasonic characterization of the microstructure.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 100, Anisotropic Grain Noise in Eddy Current Inspection of Noncubic Polycrystalline Metals.

TASK: 111

TASK TITLE: Environmentally Compliant Surface Treatments for Aerospace Alloys

TASK OBJECTIVE: Development of nonchromate surface treatment corrosion protection coatings for future aircraft coatings and incorporation of results from the task into coating systems intended for use beyond 2003.

SCIENTIST: Natalia Voevoedina

DESCRIPTION OF WORK:

The Air Force requires development of environmentally benign corrosion resistant surface treatments for aluminum skinned aircraft as a replacement for chromate-based surface treatments. Sol-gel-based surface treatment coatings offer a number of advantages, most important of which is the ability to utilize a wide variety of coating formulations, which may contain various organosilane coupling agents in combination with several metal alkoxides. Two sol-gel protective coating systems containing oxides of Si and Zr were investigated on 2024-T3 aluminum alloy coupons to as a possible nonchromate surface treatment. These coatings were also modified by adding corrosion inhibitors and surfactants.

Corrosion prevention is an extremely important top-level requirement, due to the longevity of the USAF fleet, and these coating systems must meet requirements more stringent than the commercial sector. The High Performance Aircraft Coatings Systems (HPACS) Program addressed this need for improved coating systems by evaluating commercially available, off-the-shelf coating system. The corrosion resistant performance of eight different coating systems was evaluated by investigating the coating barrier properties to immersion using Electrochemical Impedance Spectroscopy (EIS).

The prevention of pitting components in aerospace aluminum alloys with protective sol-gel coatings requires a thorough understanding of pit formation of pit formation kinetics and morphology developments in such surface systems. This study reports results of chemical and electrochemical methods of pitting corrosion tests for bare and sol-gel coated Al 2024-T3 alloy.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 109, Environmentally Compliant Surface Treatments for Aerospace Alloys.

TASK: 112

TASK TITLE: Electrochemical Test and Evaluation of Advanced Aircraft Coatings

TASK OBJECTIVE: To develop enabling electrochemical test and evaluation analytical technology for the new coatings systems. The Air Force requires development of advanced coatings which provide corrosion protection for aircraft surfaces throughout a 30-40 yr. Lifetime, and results from this task will be incorporated into coating systems beyond 2003.

SCIENTIST: Carol S. Jeffcoate, Ph.D.

DESCRIPTION OF WORK:

This report details three different experimental investigations. The first is an investigation into the viability of a sol-gel surface treatment for aircraft coating was made by electrochemical and weathering evaluation. Three complete coating systems were prepared with varying metal surface treatments including Alodyne, sol-gel and phosphate brightner treatment. The sol-gel performed very well in both electrochemical and weathering testing when compared with the system incorporating the chromate containing surface treatment of Alodyne™.

The second experimental investigation looked at the chemical effect of military specification hydraulic fluid on aluminum alloys and how any changes in the surface chemistry altered the corrosion behavior of the alloys. Initial results have shown that contamination of aluminum 2024-T3 with military specification hydraulic fluid lowered the pitting potential when the substrate was

later exposed to a conductive aqueous electrolyte. This indicated that the substrate is detrimentally effected by the hydraulic fluid and would be more prone to pitting corrosion under normal exposure conditions. Electrochemical impedance spectroscopy was also used to assess the electrochemical behavior of the contaminated samples.

Finally, the last experimental investigation detailed in this report addresses an on-going look at accelerated weathering systems when applied to aluminum substrates and the coatings associated with Air Force applications. Only preliminary results are so far available, as this project is an on-going effort. The accelerated weathering system to which coatings have so far been exposed is the modified salt spray, or Prohesion™, testing. The samples were scribed prior to exposure and monitored with electrochemical impedance spectroscopy, total reflectance spectroscopy, visual observation and gloss measurement at intervals of 1000 hours exposure.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 108, Investigation into the Corrosivity of Hydraulic Fluid, the Role of Sol-Gel as a Barrier to Atmospheric Corrosion of Aluminum and the Effect of Accelerated Weathering on Coatings.

TASK: 113

This task was canceled.

TASK: 114

TASK TITLE: Investigations of Fracture in Intermetallic Alloys

TASK OBJECTIVE: Explore new theories of the ductile-brittle transition and fracture initiation in intermetallic alloys via a combined theory and experimental approach.

SCIENTIST: Yong Qian Sun, Ph.D.

DESCRIPTION OF WORK:

The research documented in this report is a continuation of the research contained in the report for the previous task. The previous report detailed experimental and theoretical studies of the deformation properties of single crystal NiAl in the [001] orientation, with a particular emphasis on the use of the electrical resistance as a probe for the dislocation formation process in specimens undergoing dynamic mechanical loading. This follow-on research is a comparative study with the same experimental techniques on $Ni_3Al$, a material with very different deformation properties than NiAl.

The experimental research has re-demonstrated the well-known anomalous yielding characterizing $Ni_3Al$. The tensile tests on the specimens with large aspect ratios have shown that the yield point is well-defined and that there is no discernible microplastic yielding in the nominally plastic regions of deformation.

In-situ electrical resistance measurement has shown that for $Ni_3Al$ in the [001] orientation the resistance increases linearly with elongation in the elastic and plastic regions of deformation, the rate in the plastic regime being slightly larger than that in the elastic regime. This is in remarkable contrast to NiAl in which the rate of resistance increase jumped abruptly at the yield point. Origin for the differing behavior between $Ni_3Al$ and NiAl in the electrical resistance is still unknown and more research is needed.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 80, Tensile Tests of $Ni_3Al$ Single Crystals Monitored by Electrical Resistance Measurement.

TASK: 115

TASK TITLE: Molecular Modeling of Electronically Conjugated Polymers

TASK OBJECTIVE: To understand the electronic structures of new conjugated polymeric materials intended for electronic and opto-electronic applications in AF systems.

SCIENTIST: Xiaofeng Duan, Ph.D., Duans QCC, Inc.

DESCRIPTION OF WORK:

Significant effort has been placed on designing and synthesizing symmetric ground state polymers incorporating squaric acid moieties in the polymer backbone. Polymer syntheses in our laboratory and others have been hampered in obtaining well defined materials due in part to substantial mixtures of 1,2- and 1,3-linkages. The purpose of this task was to determine the relative stabilities of 1,2- vs. 1,3-squarates in order to understand the thermo-dynamics of these electronically interesting materials. The geometries of squarates with thirteen organic functional groups were fully optimized at both AM1 and RHF/6-31G* levels of theory and then the energy difference between 1,2- and 1,3-isomers was obtained at the MP2/6-31G* level. Generally, fused rings are required for the 1,3-isomers to be the more stable compounds, and trends are consistent with aromatic and charge stabilization concepts.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 112, Theoretical Calculations to Determine the Relative Stabilities of 1,2 vs. 1,3 Symmetric Ground State Squarates.

TASK: 116

TASK TITLE: Theoretical Study of Atomic Exchange Mechanisms During Molecular Beam Epitaxy

TASK OBJECTIVE: Develop theoretical and analytical models to describe important Molecular Beam Epitaxy (MBE) growth phenomena that arise due to atomic exchange mechanisms.

SCIENTIST: Stewart Harris, Ph.D.

DESCRIPTION OF WORK:

This report describes the formulation of a theoretical model that describes the growth of AlGaAs at temperatures for which the exchange of Al and Ga occurs with Al replacing Ga in the

layer immediately below. The qualitative features that this model emphasizes have been matched to computer simulation studies carried out in conjunction with the work reported.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 84, Theoretical Study of Atomic Exchange Mechanisms During Molecular Beam Epitaxy (MBE).

TASK: 117

TASK TITLE: Electronic Properties of Wide Bandgap Semiconductors

TASK OBJECTIVE: Evaluate and compare wide bandgap semiconductor materials and assess their usefulness for electronic and optical devices requiring wide bandgap materials such as high power microwave transistors and blue light emitters.

SCIENTIST: Ikai Lo, Ph.D.

DESCRIPTION OF WORK:

The electronic properties of $ZnS_{0.06}Se_{0.94}/Zn_{0.2}Cd_{0.8}Se$ quantum wells have been investigated by the Shubnikov-de Haas measurements for magnetic fields up to 8.5T and at the temperature about 1.2K. The samples were designed by the author, Ikai Lo, and grown by R.C. Tu of National Cheng Kung University with the molecular beam epitaxy, located at Chung-Shan Institute of Science and Technology. The Shubnikov-de Haas measurement was performed on $ZnS_{0.06}Se_{0.94}/Zn_{0.2}Cd_{0.8}Se$ quantum wells with the red light illumination at low temperature. Findings show that the electron density of two-dimensional electron gas in the $Zn_{0.2}Cd_{0.8}Se$ well increased with decreasing spacers thickness for the non-illuminated samples. After the illumination, it decreased and reached a saturated value after a long time exposure. The negative persistent photoconductivity is exhibited on all of the quantum well samples. The sample which has the highest electron density in the well shows the greatest saturated reduction. The negative persistent photoconductivity effect was, for the first time, observed in II-VI semiconductor compounds.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 85, Electrical Properties of Wide Band-Gap Semiconductors.

TASK: 118

TASK TITLE: Processing and Characterization of High-Performance Polymeric Materials for Space and Rocket Applications

TASK OBJECTIVE: Provide a fundamental understanding of the structural/property relationship of high-performance polymeric systems identified as leading candidates for use in rocket and space applications. The benefits from this study will be a more thorough understanding of the properties which result from various modifications to the chemical structure of the material and the ability thereby to tailor that material for optimum performance.

SCIENTIST: Angel Romo-Uribe, Ph.D.

DESCRIPTION OF WORK:

This report compiles the results of an investigation on the microstructure, morphology, rheology and flow behavior of (a) liquid crystalline materials for non-linear optical applications, and (b) high-performance macromolecular systems for rocket and aerospace applications. The aim was to understand the properties which result from various modifications to the chemical structure and to identify processing conditions for optimum performance. The results of the investigation in part (a) showed that control of the chemical architecture dictates the performance of these materials under controlled flow conditions. In part (b) a number of high-performance materials were investigated: (i) hybrid thermoplastics and elastomeric materials, developed at Dr. J.D. Lichtenhan, Phillips Lab., Edwards AFB, (ii) crosslinkable thermoplastics developed in collaboration with Prof. D. Martin (U. of Michigan), and (iii) liquid crystalline polymers synthesized at Prof. C.D. Han Laboratory (U. of Akron). The investigation identified the influence of morphology and macromolecular architecture on optimum processing conditions.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 86, Processing and Characterization of High-performance Polymeric Materials for Space and Rocket Applications.

TASK: 119

TASK TITLE: Synthesis of multi-dimensional fluorene-containing chromophores showing upconverted emission in the blue.

TASK OBJECTIVE: The synthesis and structural characterization of novel multi-dimensional model compounds, monomers, and polymers with large two-photon cross-sections which exhibit upconverted emission in the blue.

SCIENTIST: Ram Kannan, Ph.D.

DESCRIPTION OF WORK:

Syntheses of nine fluorene derived, two-photon absorbing chromophores are reported. These chromophores incorporate in their structure, an electron donor group and an electron acceptor group. In all nine compounds, the donor group is a diaryl amino function, and the acceptors are benzothiazole in most of the compounds. In four of these compounds, the donor and acceptor are arranged in more than one dimension. Most of these compounds were designed to show the upconverted emission in the blue in response to an 800 nm laser. Some attempts to produce a water-soluble chromophore are also detailed.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 122, Synthesis of Fluorene Derived Two Photon Absorbing Dyes.

TASK: 120

TASK TITLE: Investigation of Advanced Metallic Composites

TASK OBJECTIVE: To develop an understanding of the relationships between the composition and microstructure of aluminum matrices, the character of the particle/matrix interfaces, and composite properties in advanced metallic composites.

SCIENTIST: Awadh B. Pandey, Ph.D.

DESCRIPTION OF WORK:

In this investigation, intrinsic as well as extrinsic toughening mechanisms were utilized to improve the toughness of DRA composites. A powder metallurgically processed "control" DRA consisting of 7093 Al/15 vol.% SiC (10 μm) was selected as a base material. The aluminum particles were of different size. Volume fraction and composition were introduced in the DRA blend to produce ductile phase toughened composites using a powder metallurgy process. These composites were heat treated in the underaged and slightly over-aged conditions. Tensile and fracture toughness, $J_{Ic}$, tests were then performed on these composites to evaluate the influence of size, volume fraction and composition of the ductile phase on the crack initiation and growth toughness of the composites. The existing technique for J-integral measurement was also reevaluated for the small scale yielding condition. Crack initiation and growth toughnesses of most of the ductile phase toughened composites were considerably higher than the "control" DRA, indicating the advantage of ductile phase addition in the DRA. The damage ahead of crack tip was examined to provide insight into the fracture micro-mechanisms. Improvement in the initiation toughness of these composites was explained in terms of the change in the stress state due to the aluminum particles. The aluminum particles being in the crack-divider configuration in the composites can induce a transition from plane strain to plane stress condition. The increase in the crack growth toughness was discussed using crack bridging and crack trapping mechanisms.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 107, Effect of Aluminum on the Fracture Toughness of a 15 Vol.% SiCp/7093 Al Composite

TASK: 121

TASK TITLE: High Cycle Fatigue Under Biaxial Loading

TASK OBJECTIVE: To evaluate methods for modeling the life of titanium alloys under biaxial high cycle fatigue. To develop mechanistic models for predicting fatigue in titanium alloys subjected to biaxial stress states at various stress ratios under combinations of static and fatigue loading.

SCIENTIST: Rengarajan Mohan, Ph.D.

DESCRIPTION OF WORK:

It is well known that some Titanium alloys exhibit creep even at room temperature and at stresses near or below yield. Interestingly, creep deformations do occur in Ti-6Al-4V even under high cycle fatigue conditions when the mean stress is near static yield of the material and at high R ratios. In this report, the evolution of damage in Ti-6Al-4V during high cycle fatigue loading is examined through detailed scanning electron microscopy. It is shown that crystallographic cracking within a grains, which appear to be the precursor of microvoids, occurs during very early stages of deformation. The formation of many of such microvoids combined with the viscoplastic response of the material results in a cup-and-cone failure primarily through void nucleation and growth process.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 92, Failure Mechanisms in Ti-6Al-4V.

TASK: 122

TASK TITLE: Low Friction Hard Coatings Using Multilayer, Composite, and Functionally Gradient Structures

TASK OBJECTIVE: To develop new tribological films, which have multilayer, composite, and functionally gradient structures. To investigate the use of carbides, nitrides,

and diamond-like carbon (DLC) in these films for load carrying and wear resistance and solid lubricant materials to provide low friction in dry, moist and UHV environments.

SCIENTIST: Andrey A. Voevodin, Ph.D.

DESCRIPTION OF WORK:

Two types of carbon-based multilayer and composite coatings have been developed for wear protection and friction coefficient reduction: (i) functionally gradient metal/ceramic/DLC and nanolayered coatings with crystalline metal and carbide layers (about 10 nm thick) between DLC layers (about 60 nm thick); and (ii) nanocrystalline/amorphous composite coatings with 10-50 nm diameter carbide particles encapsulated in a DLC matrix. Pulsed laser deposition (PLD) was used to produce super-hard (60-70 GPa) diamond-like carbon (DLC) with a low friction coefficient and a self-lubrication. Attention was given to the improvement of the coating toughness. A hybrid of magnetron sputteing and PLD was used to deposit coatings with architectures designed to withstand 1-10 GPa contact stress. The research led to the fabrication of thin (2-3μm) DLC-based coatings for steel substrates, which could maintain a friction coefficient of about 0.1 for several million cycles of unlubricated sliding at contact pressures above 1 GPa. Super-tough characteristics have been achieved within nanocomposite coatings by controlling crack propagation. A possibility of coating operation without failure at 10 GPa contact stress was demonstrated.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 94, Multilayer and Composite Films for Sliding Wear Protection.

TASK: 123

TASK TITLE: Threshold Crack Growth Behavior in Titanium Alloys

TASK OBJECTIVE: To evaluate the near-threshold crack growth behavior in titanium alloys under high cycle fatigue and creep at high values of mean stress. To develop mechanistic models for predicting near-threshold crack growth behavior in

titanium alloys, and develop a method of determining effects of load theory on threshold fatigue crack growth values for titanium alloys.

SCIENTIST: Yuri N. Lenets, Ph.D.

DESCRIPTION OF WORK:

Engineering interpretation of the threshold stress intensity range, $\Delta K_{th}$, becomes a critical issue as damage tolerance concepts are applied to responsible applications. Recently discovered absence of the fatigue crack propagation threshold for some Ti-alloys is considered and analyzed in this effort as an important practical issue related to the mechanical properties and quality of structural materials.

Some observations on the sustained-load cracking in Ti-6Al-4V forging material tested in laboratory air were recently published by the author. The present report contains further data for the same material tested in vacuum. Three crack propagation stages were distinguished under the constant load regime in respect to the crack front shape across the specimen thickness. Individual unloading cycles (up to 100% of initial load) were shown to have no influence on the crack propagation behavior under otherwise constant load. Agreement was obtained for data generated under increasing and decreasing stress intensity. The agreement deteriorated close to the sustained-load cracking threshold and was substantially violated by switching from one pattern to another. Environmental sensitivity of the sustained-load cracking phenomenon is considered in terms of threshold stress for "no growth - growth" transition, as well as crack propagation velocity in laboratory air and vacuum.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 114, Crack Behavior in Titanium Alloys: "No-Threshold" Fatigue Crack Growth and Environmental Aspects of Sustained-Load Cracking.

TASK: 124

TASK TITLE: Silicon and Carbon Solid Source Effusion Cell Evaluation and Epitaxial Growth

TASK OBJECTIVE: The growth of high quality homoepitaxial SiC with improved dopant characteristics, low defects, high purity, and sharp interfaces. The approach will utilize solid source MBE growth process. MBE is the technique of choice for production of most epitaxial semiconductor films—highest quality, lowest cost. It is also a superior research tool. The ultra-high vacuum environment provides the opportunity to grow the most pure materials as well as the use of in-situ sensors to follow and control the growth processes. The need for high quality SiC epitaxial films was identified by the recent SiC consortium as the very highest priority. That is, the need for epitaxial films is now.

SCIENTIST: Trice Walter Haas, Ph.D.

DESCRIPTION OF WORK:

The Air Force Research Laboratory has a major program to develop high temperature, high power electronic devices for a wide variety of Air Force applications. The development of appropriate materials that can operate under these harsh conditions is one important piece of this overall program. Included in these materials development issues are the need for high quality and reproducible epitaxial films of the semiconductor silicon carbide. Silicon carbide is chosen for the basic active semiconductor material for these applications because of its many attractive properties. The growth of high quality films of this material has proved difficult and a decision was made to employ molecular beam epitaxy as a growth technique to address this need. This research is a small part of this overall effort and focused on the development of suitable solid sources for silicon and carbon to be used in this process. The program was successful in developing a silicon source cell and came up with novel carbon sources to be used in this work as well. Other issues such as a means to heat the silicon carbide to the very high growth temperatures required, techniques for surface preparation, as well as surface characterizations were addressed as well.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 158, Silicon and Carbon Solid Source Effusion Cell Evaluation and Epitaxial Growth.

TASK: 125

TASK TITLE: Equal Channel Angular Extrusion of Titanium Alloys

TASK OBJECTIVE: To establish the effect of equal channel angular extrusion (ECAE) parameters on microstructure uniformity and texture evolution.

SCIENTIST: David P. DeLo, Ph.D.

DESCRIPTION OF WORK:

Deformation behavior during Equal Channel Angular Extrusion (ECAE) was computationally modeled using finite element simulations and the results validated using experimental extrusions. The simulations demonstrated the effects of material properties and processing conditions on the occurrence of non-uniform flow. The flow softening nature of the Ti-6Al-4V material, combined with its moderately low strain rate sensitivity during high temperature deformation, caused localized flow and severe shear band formation. Thermal gradients developed during non-isothermal ECAE which exacerbated the flow nonuniformities. Die design was shown to have a significant effect on the deformation behavior. The findings from the simulations and experiments were used to design an improved technique for ECAE processing of difficult-to-work alloys in which flow localization is a problem. Further experiments to characterize the effects of the improved process are planned.

Ti-6Al-4V and Ti-24Al-11Nb powder consolidation processes were simulated using discrete element consolidation simulation software and the results were compared with experimental observations. Extensive corrections were implemented in the DECA program code. Even after the many corrections, the DECA simulation results were quite mixed. The simulated truss network was much stiffer than the experimentally measured powder compacts. Poisson behavior of the compact was inconsistent with the experimental measurements. Normalized stress intensification values from the simulations bore some resemblance to the experimental values. The structural evolution of the powder compact was affected very little by the many code modifications. Differences between the simulation results, experimental measurements, and analytical model predictions were again attributed in part to differences in the mechanisms represented in the simulation and analytical models when compared to the experimental

observations. Further compression testing of partially dense Ti-6Al-4V powder compacts is recommended to complete the analysis of stress intensification factors.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 127, Metallurgy and Advanced Metallic Materials: Equal Channel Angular Extrusion of Ti-6Al-4V and Discrete Element Modeling of Titanium Alloy Consolidation.

TASK: 126

TASK TITLE: Investigation of Advanced Metallic Composites

TASK OBJECTIVE: To develop an understanding of the influence of interface structure and composition on the properties of the interfacial region of metal matrix composites, and to relate these interfacial properties to the properties of metal matrix composites. To develop a fundamental thermodynamic approach for understanding and predicting the properties of various interfacial coatings in metal matrix composites.

SCIENTIST: Joel Phillibber

DESCRIPTION OF WORK:

The metal/fiber interface strength has a profound influence on the mechanical behavior of continuously reinforced metal matrix composites. It has been recognized that strong interfaces are required for better transverse properties while somewhat weaker interfaces are desired for axial strength and toughness. The assessment of interface strengths is commonly done through a trial and error approach as no method exists for predicting the interface strengths of a wide variety of material systems.

The goal of the current study was to develop a model for predicting metal/ceramic bond strengths using readily available thermodynamic data. The approach assumed that a small amount of the ceramic phase dissolved into the metal. The heat associated with this process was

calculated and taken to be proportional to the interface strength. Predicted bond strengths were compared to experimental data. The model appeared to predict general trends.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 124, Investigation of Advanced Metallic Composites.

TASK: 127

This task was canceled.

TASK: 128

TASK TITLE: Sensor and Imaging Techniques for Thin Film Growth and Analysis

TASK OBJECTIVE: To continue to develop data collection and manipulation capabilities for implementation of sensor and imaging techniques for thin film growth and analysis.

SCIENTIST: Donald R. Thomas, M.S., B.S.

DESCRIPTION OF WORK:

Successful growth of thin films requires accurate monitoring and control of a number of parameters. Additionally, once a film is grown, there needs to be a way to analyze and characterize that film to determine whether it was grown correctly or not. This research project presents some personal computer-based solutions for monitoring and characterizing thin films.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 132, Personal Computer Solutions for Monitoring and Characterizing Thin Films.

TASK: 129

TASK TITLE: Fundamentals of Atomic Force Microscope (AFM) Characterization of Nanocrystalline and Single Crystal Solid Lubricant and Hard Materials

TASK OBJECTIVE: To conduct research on the growth and characterization of solid lubricants and hard materials that provide low friction surfaces and/or wear protection. To design, assemble, and operate vacuum deposition equipment and an AFM for evaluation of single and nanocrystalline materials. To develop standard and AFM-based tribological tests to determine mechanical and friction/wear properties of materials on an atomic level as part of the overall research and development program in advanced tribological materials.

SCIENTIST: Josekutty Nainaparampil, Ph.D.

DESCRIPTION OF WORK:

Typically SiC films are deposited on substrates at elevated temperatures either by sputtering SiC targets or using other conventional deposition methods. To maintain substrate properties (temper, dimensional tolerance, etc.) a low process temperature is required. In this task effort, silicon carbide was formed from simultaneous sputtering of silicon and laser ablation of graphite onto substrates at room temperature. The advantage in this method lie in the individual selection of the species accelerated to optimum energy which permitted the formation of selected phases in the film. Films were formed on M50 steel substrates at biasing varied from -100 to -300 Volts resulted in different deposition rates for carbon and silicon and changes in bonding strength. The shift in the binding energies of carbon and silicon obtained from XPS analysis corresponded to the silicon carbide bonds. Chemical bonding data was correlated to microstructure and mechanical properties. Special emphasis was given to film stoichiometry control and Si/C composition ratio to achieve optimum tribological properties.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 103, a-SiC Thin Films Deposited Using Pulsed Laser Ablation of Graphite and Magnetron Sputtering of Silicon onto Steel Substrates at Room Temperature.

TASK: 130

TASK TITLE: Surface Chemistry of Lubricants, Additives, and Coatings Using Synchrotron Radiation Based Methods

TASK OBJECTIVE: To determine the nature of friction and wear of aircraft materials from a surface chemistry perspective.

SCIENTIST: Jeffrey N. Cutler, Ph.D.

DESCRIPTION OF WORK:

This report provides critical insight regarding the interaction of perfluoropolyalkylether (PFPAE) fluids and a related additive (triphenyl phosphine) with Fe-based alloys. PFPAEs are primary candidates for the development of high temperature liquid lubricants for the next generation of turbine engines because of their chemical and thermal stability. However, complex surface layers have been identified on M-50 steel samples exposed to a linear perfluoropolyalkylether (PFPAE) in the presence of air at 260°C. An understanding of the mechanisms that drive the formation of these layers is believed to be crucial for efforts to develop PFPAEs as effective lubricants. Work presented here shows that the extreme surface region contains physi-sorbed PFPAE followed by an $Fe_3O_4$ layer under which an $FeF_2$ layer which lies adjacent to the substrate. X-ray photoelectron spectroscopy (XPS) and conversion electron Mössbauer spectroscopy (CEMS) were used to unambiguously characterize these layers.

In order to improve the overall wear properties of a PFPAE oil, a soluble additive, such as triphenylphosphine, was added to the fluid. Overall, performance was improved as the triphenylphosphine decomposed on the surface, within the wear track, forming a tribofilm composed of a polyphosphate material. However, the formation and protective properties of these films were controlled by three important environmental factors. First, oxygen was required to be present in order to form the polyphosphate. Second, hydrolysis of the additive was required to drive the reaction to completion. (At low humidity, a large amount of unreacted and intermediate

material was found within the wear track.) Third, the test temperature combined with the relative humidity controlled the overall useful lifetime of the additive.

In order to gain some understanding on how this additive works, a series of tribological experiments were performed at different temperatures, relative humidities and rubbing times. The resulting coupons were examined by x-ray absorption near edge structure spectroscopy (XANES) and imaging photoelectron spectromicroscopy (MEPHISTO).

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 121, Characterization of Surface Layers Formed by Perfluoropolyalkylether Lubricants and Additives at Elevated Temperatures using X-ray Absorption Near Edge Structure (XANES) and X-ray Photoelectron Spectroscopies (XPS).

TASK: 131

TASK TITLE: Sol-gel Based Surface Treatments for Aerospace Aloys

TASK OBJECTIVE: To investigate the utility of chemically tailored, corrosion resistant sol-gel based nonchromate surface treatments for future aircraft coating systems. Results from this task will be incorporated into coating systems beyond 2003.

SCIENTIST: Nathan Grebasch

DESCRIPTION OF WORK:

Research focused on several coating related problems which could be addressed by employing sol-gel chemistry. (Sol-gel is a method by which a metal alkoxide, a metal containing an ether linkage, is hydrolyzed to form a hydroxyl intermediate (-OH) which undergoes a condensation reaction to form a metal oxygen to metal bond (-M-O-M-).

The goal of using sol-gel technology in a coatings program is that some sol-gels have been shown to covalently bond to aluminum based substrates. Covalent bonding could offer a new mechanism for coating adhesion to the alloy instead of hydrogen bonding and mechanical interlocking.

Another benefit to sol-gel technology is that it is an environmentally friendly process which is water based with the only waste generated being a non-toxic glass. This is in direct contrast to the current state of the art which is an acidic, toxic chromate wash procedure.

In addition, sol-gel technology has the ability to form a coating which has good barrier properties to limit the diffusion of water through the coating and to the substrate surface. The ability to form a good barrier is an asset because water containing ions, especially chloride anions is the main mechanism by which aluminum alloys initiate corrosion.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 116, Sol-gel Based Surface Treatments for Aerospace Alloys.

TASK: 132

TASK TITLE: Corrosion Prevention Technology for Paint for Life Coatings Systems

TASK OBJECTIVE: To investigate corrosion initiation mechanisms in aluminum aerospace alloys - 2024, T3 - using high resolution surface analytical techniques. This includes baseline information on current surface treatments used for corrosion prevention. Successful corrosion prevent technology must be based on a thorough, fundamental understanding of corrosion phenomenon as related to aircraft systems, and includes corrosion inhibitor mechanisms. The corrosion prevention technology will be incorporated into aircraft coatings systems beyond the year 2003.

SCIENTIST: Rebecca Twite, B.S.

DESCRIPTION OF WORK:

A variety of pretreatments are currently used to prepare aluminum alloys for aerospace applications. Although an important step, the effect of the pretreatment is not very well understood on a microscopic scale. X-ray photoelectron spectroscopy, Auger electron spectroscopy, and

scanning electron microscopy are used to provide information concerning the surface state of different surface preparation techniques for aluminum 2024-T3 following ASTM D 1730. Each analyzed system produces a characteristic XPS spectrum from which the oxide layer morphology and thickness are determined. This effort showed that most aggressive pretreatment was the phosphoric acid deoxidization treatment which induced pitting in two of the three pretreatment processes. Breakdown of the oxide layer and exposure of the copper regions are cited for pit initiation.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 104, Surface Analysis of Various Methods for the Preparation of Al-2024-T3 Surfaces for Painting.

TASK: 133

TASK TITLE: Ultrasonic Quantification of Corrosion Damage in Aircraft

TASK OBJECTIVE: To predict the limits of ultrasonic quantification of corrosion damage in typical single layer aircraft structure.

SCIENTIST: William Mullins, Ph.D.

DESCRIPTION OF WORK:

An overall framework for incorporation of corrosion models into probability of failure (POF) models for the system is outlined. The approach uses the results of stochastic kinetic models for corrosion evolution to determine the morphology of the effected region. From this morphology, associated local stresses were calculated. This distribution of local stresses was then used with classical fatigue models to predict system POF. As such, corrosion could then be considered as a generalized "damage" with a quantifiable damage parameter and a relationship between this damage parameter and the physical measurables of the effected regions.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 125, Stochastic Surface Corrosion Damage Quantification.

TASK: 134

TASK TITLE: Damage Evolution under High Cycle Fatigue

TASK OBJECTIVE: To evaluate methods for detecting the evolution and growth of fatigue damage in titanium alloys subjected to high cycle fatigue. To develop mechanistic models for predicting the initiation and growth of damage in titanium alloys subjected to high cycle fatigue.

SCIENTIST: Vikram K. Kinra, Ph.D.

DESCRIPTION OF WORK:

Two problems of current technological interest to the USAF were addressed during this work. (1) Ultrasonic NDE of adhesively-bonded graphite/epoxy lap joints. A technique was developed for an in-situ measurement of the thickness and stiffness of the adhesive bond layer that joins the composite laminates (Ultrasonic NDE of transverse cracks in laminated composites). A technique was developed for the detection of transverse cracks which does not intersect (cross) any of the laminate surfaces and, therefore, cannot be detected by any of the traditional methods.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 111, Damage Evolution under High Cycle Fatigue.

TASK: 135

TASK TITLE: Processing of Electrically Conducting Nanocomposites and Electro-Optic Films for Multifunctional Materials

TASK OBJECTIVE: Production of polymeric-based materials comprised of an interpenetrating network of anisotropic metal nanoparticles and polymers. Processing and characterization of high quality films of guest-host chromophore-polymer systems and chromophore-containing copolymer systems for electro-optic applications.

SCIENTIST: Jar-Wha Lee, Syscom Technology, Inc.

DESCRIPTION OF WORK:

In this task, preparation of reflective Poly(N,N'-bisphenoxyphenylpyromellitimide) (Kapton)/silver and poly(p-phenylenebenzoxazole)(PBO)/silver composite films by utilizing template fabrication technique were successfully demonstrated. The processing scheme consisteded of initial polymer host swelling, metal precursor infiltration and chemical reduction. The results indicated that the silver(I) ions could be infiltrated into the N-methyl-pyrrolidinone(NMP)-swelled Kapton and the sulfuric-acid-swelled PBO films and converted in-situ to silver metal at the presence of sodium borohydride. The size of the silver particles formed within such a confined polymer host appeared to be at the nanometer scale. However, thus prepared silver/Kapton and silver/PBO composite films showed only the modest surface reflectivity, compared to that of the silver coated Kapton film. It is believed that the low volume percentage of silver and the surface roughness of the composite films could account for the observed modest surface reflectivity.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 99, Control of Surface Reflectivity in Metallized Polymer Film Via Template Fabrication.

TASK: 136

TASK TITLE: Molecular Dynamics Modeling of Lubricant Base Fluids

TASK OBJECTIVE: To computationally predict the temperature and pressure coefficients of viscosity of various lubricant base fluids including perfluoropolyalkyl ethers, polyalphaolefins and pentaerythritol esters.

SCIENTIST: Martin Schwartz, Ph.D.

DESCRIPTION OF WORK:

The goal of this project was to investigate the principal sites for initiation of the photolytic decomposition of linear and branched aliphatic urethanes, in order to aid in the development of new polyurethane coatings with enhanced durability.

Carbon-hydrogen and nitrogen-hydrogen room temperature Bond Dissociation Enthalpies (BDEs) were computed for the various bonds in the vicinity of the urethane linkage of a series of model compounds. It was determined that, for linear species, the BDEs varied in the order, $\alpha$-C(N)[402] < $\alpha$-C(O) [417] < $\beta$-C(N) [425] $\approx$ $\beta$-C(O) << N-H [465], leading to the prediction that the weakest bond is the C-H bond on the $\alpha$-carbon on the nitrogen side of the urethane group. Addition of a methyl group to the $\alpha$-carbon on either side of the functional group induced an increase in the BDE.

Computed reaction energy barriers for photon abstraction (by a methyl group), generally showed a good correlation with BDEs. However, the barriers for abstraction at the $\alpha$-carbons of the branched urethanes were actually lower than for the linear species, in contrast to the trend observed in BDEs. Based upon these results, it was concluded that branching of the alkyl groups in aliphatic urethanes does not enhance the photostability relative to their linear counterparts.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 138, Computational Study of Bond Dissociation Enthalpies and Hydrogen Abstraction Energy Barriers in Model Urethanes.

TASK: 137

This task was canceled.

TASK: 138

TASK TITLE: Fracture and Fracture Behavior of Fibrous Monolithic Ceramics

TASK OBJECTIVE: To document the high temperature fracture behavior in highly textured ceramics.

SCIENTIST: James M. Staehler, Ph.D.

DESCRIPTION OF WORK:

Four state-of-the-art ceramic matrix composite materials were evaluated as potential replacement parts for the divergent flaps and seals of a turbofan engine's exhaust nozzle. Flap inserts fabricated from each of the four ceramic matrix composites were ground tested on an F110 engine by General Electric, Evendale, Ohio. Following ground testing, each of those parts were then evaluated for signs of degradation and loss in tensile properties. The results of the post-ground-test evaluations are presented in this final report. Visual, optical, scanning electron microscopy, and ultrasonic c-scans were used to document any distress to the parts. Each of the flap inserts were ultimately cut into tensile specimens and tested. Two of the four composites, a Nicalon/SiNC and a Nicalon/C, showed no significant signs of distress or loss of tensile properties as a result of the ground testing. Two others, a Nicalon/Al $_2O_3$ and a Nextel 720/AS, did experience edge cracking as a result of the thermal gradients encountered during afterburner lights. New flap inserts comprised of the two promising composites were subjected to additional ground testing. After accumulating over 60% of the intended design life, the Nicalon/SiNC flap had to be removed because of cracking. The cause of the cracking was felt to be related to hot-streaking during afterburner lights and severe temperatures which may have been experienced by the part.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 129, Evaluation of CMC Divergent Flaps Following Ground Testing on F110 Turbofan Engines.

TASK: 139

TASK TITLE: Low Friction Hard Coatings Using Multilayer, Composite, and Functionally Gradient Structures

TASK OBJECTIVE: To develop new tribological films, which have multilayer, composite, and functionally gradient structures. To investigate the use of carbides, nitrides, and diamond-like carbon (DLC) in these films for load carrying and wear

resistance and solid lubricant materials to provide low friction in dry, moist and UHV environments.

SCIENTIST: Andrey A. Voevodin, Ph.D.

DESCRIPTION OF WORK:

Coatings that offer protection from wear, low friction coefficients, and corrosion resistance are required for many applications in modern aerospace systems. To meet the requirements of these applications, it is necessary to create new materials by adjusting chemistry and microstructure. To achieve significant advancements in coating properties, we must go beyond layer/single phase materials. Functionally gradient, multilayer, and composite coatings permit blending of properties traditionally considered mutually exclusive, for example, hardness and toughness. To facilitate growth of these types of coatings, improved deposition techniques must be developed. This report focuses on the development of new coating materials based on metals (Ti and W), carbides (TiC and WC), diamond-like carbon (DLC), carbon nitride (CN), and transition metal dichalcogenides ($WS_2$), which are incorporated in functionally gradient, multilayer, and nanocomposite architectures, including three-phase WC/DLC/$WS_2$ nanocomposites targeted for aerospace applications. The results in the development and use of magnetron assisted pulsed laser deposition process for the growth of these advanced coatings have also been provided.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 131, Low Friction Hard Coatings Using Multilayer, Composite, and Functionally Gradient Structures.

TASK: 140

TASK TITLE: The Role of Mechanics in Micro Electro Mechanical Systems (MEMS) Technology

TASK OBJECTIVE: Provide an assessment of the state of the art of applied mechanics in the field of MEMS technology and define the research needs in mechanics to predict the life and strength of MEMS devices.

SCIENTIST: Roberto Ballarini, Ph.D.

DESCRIPTION OF WORK:

This project involves (1) a review of recent studies of the mechanical behavior of polycrystalline silicon used to fabricate microelectromechanical systems (MEMS) devices, (2) the development of original theoretical models and experimental techniques that will lead to improved understanding of such behavior, and (3) suggestions for future research.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 130, The Role of Mechanics in Microelectromechanical Systems (MEMS) Technology.

TASK: 141

TASK TITLE: Durable/Cleanable Coating Development

TASK OBJECTIVE: The Air Force requires development of advanced aircraft coatings which incorporate high durability components and cleanable, stain-resistant formulations. The objective of this task is to develop enabling durable/cleanable coatings for future aircraft coating systems so that results from this task can be incorporated into coating systems beyond 2000.

SCIENTIST: Stuart Croll, Ph.D. and Joel Johnson

DESCRIPTION OF WORK:

The objective of this task was to aid in the development of an aircraft topcoat system with a focus on excellent long term outdoor weatherability, service durability, cleanability, and stain-resistance. The results of this work were intended to show the effect of different raw materials (polymer resins and extender pigments) and formulation parameters in obtaining a coating that meets the "Durable, Cleanable Requirements Document" specifications. The results of the commercial polyurethane resin study performed indicate that the use of tetramethylxylene diisocyanate (TMXDI) type polyisocyanates are detrimental to coating performance due to

incomplete curing under the imposed conditions. The most promising resin system was comprised of a polyester polyol resin (Bayer 670A-80) reacting with a hexamethylene diisocyanate type polyisocyanate (Bayer N75). The results from the commercial extender pigment study indicate the importance of formulation by pigment volume concentration and not exceeding the critical value for this concentration. The best results were obtained by the use of PPG Lo-Vel HSF silica flatting agent incorporated into the most promising resin system at a pigment volume concentration of 0.19. Details of the coating formulations are included along with performance results for both the resin and extender pigment study.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 135, Durable/Cleanable Coating Development.

TASK: 142

TASK TITLE: Project Management/Administration

TASK OBJECTIVE: To provide for those project activities necessary to establish project task orders and overall contract management and administration.

SCIENTIST: Nagu Nagarajan

DESCRIPTION OF WORK:

The contributive research and development project required extensive management and administration activities that were not readily charged to a specific task. These activities fell into three general categories:

1. Those contract management administrative requirements to establish planning and control procedures that applied to the project as a whole. Examples are status reporting, project management meetings, and other general overall project reporting.

2. Those management activities required to establish each of the task assignments. These activities could not be charged to the task since the task was not yet approved during this phase.

3. Recording and reporting the performance and cost for the overall management and administrative activities.

This task provided project management/administration from 16 December 1997 through 15 December 1998.

TASK: 143

TASK TITLE: Organic Aircraft Coatings

TASK OBJECTIVE: Formulation of organic coatings with state-of-the-art commercially available raw materials. These coatings will be the bases for a fundamental study on mechanisms and degradation.

SCIENTIST: George Pacinda

DESCRIPTION OF WORK:

The mission of the WUD-2 Task I Mechanisms of Coatings Degradation is to create revolutionary new coatings technology for Air Force applications using a basic research approach to coatings science. Research efforts have centered on both physical and chemical degradation studies, carried out on model formulated coatings of known commercial and chemical compositions. Our efforts have been to determine what structural changes in the coatings relate to both improved durability and improved cleanability.

Model formulated urethane coatings were prepared using commercially available materials and processed on Al-2024-T3 substrates. Baseline physical properties testing was performed (hardness, low temperature impact resistance, color, gloss, cleanability, etc.) prior to accelerated artificial weathering in both QUV-A (340 nm peak), QUV-B (313 nm peak), and Xenon Arc (Atlas Ci-35A) weatherometers.

The objective of this task was to aid in the development of an aircraft topcoat system with a focus on excellent long term outdoor weatherability, service durability, cleanability, and stain-resistance. The results of this work were intended to show the effect of different raw materials (polymer resins and extender pigments) and formulation parameters in obtaining a coating that meets the required specifications.

The use of High Irradiance QUV-A (1.35 W/m2) gives rapid, repeatable chalking and coating degradation not only faster than standard QUV-A exposures, but also more realistic than standard QUV-B exposure. Chalking is much more pronounced.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 160, Mechanisms of Coatings Degradation In-Durable / Cleanable Coatings.

TASK: 144

TASK TITLE: Fatigue Crack Growth Thresholds

TASK OBJECTIVE: To evaluate several methods for conducting tests on titanium alloys to establish the influence of prior load history on the threshold for fatigue crack growth.

SCIENTIST: Florian Holzapfel

DESCRIPTION OF WORK:

This task was aimed at experiments which would provide a set of data for the enhancement of the "Engine Structural Integrity Program (ENSIP)" in terms of high cycle fatigue (HCF). Hence, two sets of experiments were conducted. The first set of experiments dealt with methods for conducting tests on titanium alloys to establish the influence of prior load history on the threshold for fatigue crack growth. The second set of experiments were conducted to validate the first test series dealing with frequency and mean stress effects on HCF.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 113, Fatigue Crack Growth Thresholds.

TASK: 145

TASK TITLE: Fundamentals of Atomic Force Microscope (AFM) Characterization of Nanocrystalline and Single Crystal Solid Lubricant and Hard Materials

TASK OBJECTIVE: To conduct research on the growth and characterization of solid lubricants and hard materials that provide low friction surfaces and/or wear protection. To design, assemble, and operate vacuum deposition equipment and an AFM for evaluation of single and nanocrystalline materials. To develop standard and AFM-based tribological tests to determine mechanical and friction/wear properties of materials on an atomic level as part of the overall research and development program in advanced tribological materials.

SCIENTIST: Josekutty Nainaparampil, Ph.D.

DESCRIPTION OF WORK:

Atomic Force Microscopy (AFM) is used to study low friction structures formed on single crystal zinc oxide as a result of annealing. Zinc oxide thin films deposited in this laboratory showed low friction ( ~ 0.2) and long wear life (over one million cycles) in humid air at room temperature. Research into the mechanisms for this low friction behavior, far exceeding the life of typical solid lubricants (e.g. MoS2 and graphite) led to the present work which focuses on the nanotribology of single crystal ZnO surfaces. Thermal annealing was used to cause surface reconstruction and defect formation. Etch pits were formed on the ( 1 0 1 0 ) surface and roughening or reconstruction occurred on the ( 0 0 0 1 ) surface. These pits and roughened areas showed low friction that could be originating from interactions of defects and restructured crystal faces due to adsorbates. Adhesion and relative contact stiffness were not significantly different between friction contracting regions. The results of LFM analysis of the different single crystal surfaces are presented here.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 141, Nanotribology of annealed single crystal ZnO surfaces: Restructuring at high temperature

TASK: 146

TASK TITLE: Processing and Characterization of High-Performance Polymeric Materials for Space and Rocket Applications

TASK OBJECTIVE: The objective of this task is to provide a fundamental understanding of the structure/property relationships that exist for high-performance polymeric materials identified as leading candidates for use in rocket and space applications. The benefits from this study will be a more thorough understanding of the properties of specific thermoplastics which results from various modifications to the chemical structure of the materials and the stability thereby to tailer this class of materials for optimal performance.

SCIENTIST: Hong Guk Jeon, Ph.D.

DESCRIPTION OF WORK:

Hybrid organic-inorganic materials prepared from Polyhedral Oligomeric Silsequiozane (POSS) reagents have received an increasing amount of attention due to their many desirable properties coming from both the inorganic and organic components. Recently, we synthesized and characterized norbornyl-POSS hybrid random copolymers possessing either cyclonhexyl corner groups (CyPOSS) or cyclopentyl corner groups (CpPOSS). Owing to the POSS-reinforcement of the parent polymer (polynorbornene), thermal stability and mechanical properties have been found to be enhanced by increasing the mole fraction of POSS macromers. More interestingly, the type of cycloalkyl group present in the POSS macromer affects the ordering of POSS macromers in polynorbronene, which likely causes the modification of physical properties. In order to further understand the structure-property relationships, wide-angle x-ray scattering and dynamic mechanical analysis have been performed on these newly developed hybrid polymers.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 145, Mechanical Relaxation and Microstructure of Poly(norborny-POSS) Copolymers.

TASK: 147

TASK TITLE: Processing of Electrically Conducting Nanocomposites and Electro-Optic Films for Multifunctional Materials

TASK OBJECTIVE: Production of polymeric-based materials comprised of an interpenetrating network of anisotropic metal nanoparticles and polymers. Processing and characterization of high quality films of guest-host chromophore-polymer systems and chromophore-containing copolymer systems for electro-optic applications.

SCIENTIST: Jar-Wha Lee, Ph.D., Syscom Technology, Inc.

DESCRIPTION OF WORK:

This research study tested a solution processing scheme for fabricating an electrically conductive Metal/Polymer NanoComposite (MPNC) fiber from a rigid-chain lyotropic liquid crystalline polymer, poly(p-phenylene benzobisoxazole) (PBO). The conductivity was introduced by incorporation of a silver metal precursors that can be blended in with the polymer host and then converted in-situ, templating the morphology of the polymer matrix and forming a continuous metal network in the polymer host. The results has demonstrated that silver metal precursors can be readily blended into PBO/PPA dope without disturbing the fiber spinning process and subsequently can be reduced by using sodium borohydride to form a highly conductive MPNC PBO fiber. Depending on the reduction process, the value of the fiber electrical conductivity as high as 6000 S/cm was observed. Most importantly, since the metal network was embedded in the polymer matrix, the metal to polymer interface adhesion was dramatically improved via an interlocking mechanism. In contrast, the commercially available metallized fiber suffers from potential fatigue or delamination in thermal or mechanical cycles owing to the metals being coated only on the surface of the polymer fiber. It is expected that the metal-containing PBO fiber will have advantages over metal wires in weight savings, mechanical flexibility, durability and strength.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 207, Processing of Electrically Conducting Nano Composite Polymer Fibers.

TASK: 148

TASK TITLE: Nondestructive Microstructure Characterization of Titanium

TASK OBJECTIVE: To develop nondestructive evaluation techniques necessary that are capable of uniquely characterizing microstructure in alloys of titanium.

SCIENTIST: Peter B. Nagy, Ph.D.

DESCRIPTION OF WORK:

The main goal of this effort was to investigate the feasibility of exploiting the unique eddy current grain noise observed in titanium alloys for the purposes of nondestructive materials characterization. The main achievements of this effort are that we have (i) experimentally demonstrated the very strong electrical grain noise in titanium alloys, (ii) theoretically explained the physical mechanism responsible for this contrast, (iii) used analytical, finite element simulation, and experimental methods to investigate the lateral resolution of eddy current microscopy, and (iv) developed and verified optimization procedures that assure the best imaging resolution for microstructural materials characterization. It is shown that electric anisotropy exhibited by non-cubic crystallographic classes of materials can play a very similar role in electromagnetic materials characterization of polycrystalline metals to that of elastic anisotropy in ultrasonic materials characterization. Titanium is one of the few structural metals of practical importance, especially in aerospace applications, which preferentially crystallizes in hexagonal symmetry and therefore exhibits strong electrical anisotropy. At the same time, titanium tends to form a rather coarse, locally textured microstructure characterized by the presence of large colonies of hexagonal alpha grains featuring similar orientation. The fracture resistance of the material is strongly affected by this microstructure therefore is a continued need for new nondestructive evaluation techniques that are capable of both imaging and quantitatively characterizing this microstructure. It was found that the lateral resolution of eddy current imaging is ultimately limited by the probe-coil geometry and

dimensions, but both the inspection frequency and the phase angle can be used to optimize the resolution, to some degree, at the expense of sensitivity. Although eddy current imaging is still in its infancy, a direct comparison of 5-MHz eddy current and 40-MHz acoustic microscopic images of the sam coarse-grained Ti6Al-4V sample indicated that the same features can be observed by both methods at approximately the same resolution level. It is expected that in the future eddy current microscopy can be further enhanced by the introduction of special high-resolution, microscopic probe-coils which will make it a truly unique materials characterization tool especially well suited for microstructural evaluation of titanium alloys.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 144, Theoretical and Experimental Investigations of Eddy Current Microscopy

TASK: 149

TASK TITLE: Evaluation of High Performance Polymeric Materials with Solid State Nuclear Magnetic Resonance (NMR) Spectroscopy

TASK OBJECTIVE: The objective of this research is to utilize NMR Spectroscopic techniques in the evaluation of high performance polymeric and composite materials. Specifically, a class of exfoliated silicate modified thermoset resins and addition polyimides are of interest.

SCIENTIST: Brett A. Cowans, Ph.D.

DESCRIPTION OF WORK:

A preliminary investigation is made into the cure and degradation chemistry of AFR700 type resins. The cure chemistry of the AFR700 resin is complex but may be similar to that observed for bismaleimide type resins. Recent literature suggests that the reverse Diels-Alder reaction may not occur at the norbornyl end-group, but that a biradical mechanism takes place. The specific type of cross-links formed in the AFR700 resin remains unclear as well as whether the norbornyl groups are involved in Michael addition reactions with the amine end-groups. Fully

labeled AFR700 shows very little effect by NMR when hydrolyzed at 200C, however, an oligomer formulation shows that terminal succinimide groups are readily hydrolyzed to amide or amic acid.

The Tecmag spectrometer has been adjusted to provide acceptable performance. Several problems continue to plauge the spectrometer and procedures for troubleshooting and repair have been discussed. Recommendations are made for operation under more stringent environmentally controlled conditions.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 140, Solid-State Nuclear Magnetic Resonance Spectroscopy of Polymeric Materials.

TASK: 150

TASK TITLE: Theoretical Study of Heterointerface Formation in Strained and Unstrained Semiconductor Thin-Film Material Systems

TASK OBJECTIVE: Develop computer models for desorption, segregation, and heterointerface formation during Molecular Beam Epitaxy (MBE) growth of strained and unstrained III-V materials. Use these models to find the optimal MBE growth conditions to obtain atomically abrupt interfaces.

SCIENTIST: Krishnamurthy Mahalingam, Ph.D.

DESCRIPTION OF WORK:

Transmission electron microscopy (TEM) studies were performed on a variety of arsenide and antimonide based III-V compound semiconductor heterostructures grown by molecular beam epitaxy. The systems examined include GaAs/AlGaAs, GaAs/InGaAs and InAs/InGaSb heterostructures. The applicability of different imaging techniques, such as: (200) dark-field imaging, (000)-(200) interference imaging and chemical lattice imaging, to each of these system is investigated. It is observed that the (200) dark-field imaging technique is adequate for examining interface roughness and compositional inhomogeneities at a resolution approaching 0.5 nm. The contrast differences between different layers observed in these images is explained in terms of a

kinematical calculation of the (200)-intensity ratio for the constituent layers. The (000)-(200) interference imaging technique is useful for measuring thicknesses of extremely thin layers (< 16 monolayers of GaAs/AlGaAs system). A high-resolution TEM image simulation study performed for the InAs/InGaSb system indicates that the chemical lattice image technique is not suited for this system. This is explained in terms of the similarity in the dynamical behavior of the (200) and (220) reflections for both InAs and InGaSb.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 142, Transmission Electron Microscopy of III-V Compound Semiconductor Heterostructures.

TASK: 151

TASK TITLE: Deep Levels in Silicon Carbide

TASK OBJECTIVE: Determine the effect of polytype on the deep levels present in bulk grown and epitaxial silicon carbide and evaluate possible dopants for the formation of semi-insulating SiC.

SCIENTIST: Andrew O. Evwaraye, Ph.D.

DESCRIPTION OF WORK:

The shallow acceptors in p-type silicon carbide of 4H- and 6H- polytypes were studied using Thermal Admittance Spectroscopy (TAS). Aluminum produces two activation energy levels in 4H-SiC:Al. The ground state energies are $E_V$ + 0.212 eV (hexagonal) and $E_V$ + 0.266 eV (Cubic). Boron in 6H-SiC:B produces three activation energy levels at $E_V$ + 0.27 eV (h), $E_V$ + 0.31 eV ($k_1$), and $E_V$ + 0.38 eV ($k_2$). From these results, we conclude that acceptors establish activation energy levels that are polytype dependent.

Comparative studies of Chemical Vapor Deposition grown films and of Sublimation Sandwich Method films. Based on the data, the SSM samples behave more like bulk samples than thin films grown by CVD.

Heavily doped 4H-SiC samples ($N_D$-$N_V$ = $10^{19}$ $cm^{-3}$) were heat treated at 1900°C for one hour. The atomic force micrograph of the annealed samples showed long furrows running along one direction with small pits along the furrows. An Auger analysis of the pits showed the pits were rich in sodium, oxygen, silicon, carbon, and chlorine.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 137, Thermal and Optical Studies of 4H- and 6H-SiC Single Crystals.

TASK: 152

TASK TITLE: Structural and Nonstructural High Performance Polymers

TASK OBJECTIVE: Synthesis of high performance polymers for Air Force applications.

SCIENTIST: Narayanan Venkatasubramanian, Ph.D.

DESCRIPTION OF WORK:

This report relates to the syntheses and characterization of some novel basic thermoset monomers using known mehtodologies, with the objective of subsequently evaluating their suitability as reactive plasticizers for the processing of thermoset rigid-rod composite foam structures, with 2-sulfo-poly (p-phenylenebenzobisimidazole) (SPBI) as the dispersed phase. One of the target monomers, 1, 3-bis (3-phenylethynylpyridine-3'-oxy) benzene was synthesized via the palladium (II) catalysed cross-coupling reaction between 1,3-bis (3-phenylethynylpyridine-3'-oxy) benzene and phenylacetylene in good, isolated yield. The DSC analysis of the thermoset monomer under nitrogen revealed a melting endotherm at 103°C, a low glass transition temperature (Tg) at 9°C upon rescan after heating to 130°C and cure exotherm onset temperature of 300°C. Preliminary results indicated that a 50/50 w/w SPBI/thermoset blend could be compatibilized utilizing the acid-base interaction between the rod and the matrix. Synthesis of the other target monomer, 1, 3-bis(ethynylpyridine-3'-oxy) benzene was explored via the intermediacy of its bisacetone adduct formed from 1,3-bis(3-brommopyridine-3'-oxy)benzene and 2-methyl-3-butyn-2-ol and the base-catalysed deprotection of the adduct to form the bis(terminal alkyne).

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 155, Novel Basic Thermosets For Compatibilization With and For In Situ Plasticzation of Rigid-Rod Polymers.

TASK: 153

TASK TITLE: Analysis and Enhancement of the Optical Limiter Numerical Test-Bed Simulation Software

TASK OBJECTIVE: To update, refine, and enhance the current beam propagation simulation program, "Optics" as a tool for analyzing the interactions between laser energy and nonlinear materials for laser hardening applications.

SCIENTIST: Chiu-Tai Law, Ph.D. and Mark O'Neil

DESCRIPTION OF WORK:

The performance and capabilities of the original beam propagation simulation code, know as "optics", have been greatly enhanced. Particularly, its speed in modeling pulse propagation in reverse saturable absorptive (RSA) media which requires 4 dimensional simulation is drastically improved. "Optics" can now simulate the propagation of a laser beam within a graded concentration limiter. An adpative grid based on geometric optics has been developed to accommodate the size reduction of a focused beam. Although "optics" does not limit the input beam profile, the procedure for profile and parameter generations can be complicated. Additional utilities have been implemented to alleviate users' burden. They allow the generation of arbitrary input profiles with radial symmetry and corresponding parameters that are compatible with "optics".

The enhanced code has been compared to known analytical approximations for 4 different designs of graded concentration limiters. In each design, 4 input pulse shapes have been tested. Comparisons show close agreement between simulations and analytical approximations, except in the region near the focus. Other simulations have been performed, including the design of stepped concentration limiters and limiter performance for input energy below the designed level. Promising results that exhibit desirable limiting behavior may be obtained.

Modifications to the existing software were performed to provide a more powerful tool for evaluating non-linear materials and optical systems for laser hardening applications.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 133, Enhanced Version of "Optics", A Beam Propagation Simulation Code and Volume 134, Analysis and Enhancement of the Optical Limiter Numerical Test-Bed Simulation Software.

TASK: 154

TASK TITLE: Environmentally Compliant Surface Treatments for Aerospace Alloys

TASK OBJECTIVE: Development of nonchromate surface treatment corrosion protectioncoatings for future aircraft coating systems, and results from this task will be incorporated into coating systems beyond 2003.

SCIENTIST: Natalia Voevodina

DESCRIPTION OF WORK:

The search for new coatings to protect aerospace structural aluminum alloys against environmental corrosion remains the challenge provided by the current requirements seeking 30+ service years for aircraft in Air Force use. To achieve such a long service life, functional layers of surface treatment, primer, and top-coat are normally included into the protective coatings system on aluminum alloys. The coating process typically includes surface treatment with an oxidation process, such as a chromium oxide acid conversion pre-treatment (Alodine). In order to provide a self-healing corrosion protection effect in places of possible local damage, chromates are included in the composition of either the oxide pre-treatment or the epoxy primer layers. One problem with such coatings is that over a long period of time water molecules penetrating to the primer-oxide interface break the weak hydrogen bonds of the epoxy resin hydroxyls, causing coating failure. Another problem is that the presence of chromates in the coating composition may not comply with strict environmental protection regulations.

A chromate-free sol-gel treatment was suggested as an alternative approach, where metal alkoxides are used to form strong covalent bonds with the aluminum surface. Additionally, sol-gel coatings are typically made of inorganic esters, ceramics, and organosilicates, with excellent barrier properties to corrosion currents. However, the problem of corrosion suppression in damaged places for these chromate-free coatings remains unsolved. This problem may be addressed by compositional adjustment of the sol-gel and the primer coatings, e.g. by incorporation of inorganic or organic corrosion inhibitors.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Environmentally Compliant Surface Treatments for Aerospace Alloys.

TASK: 155

TASK TITLE: Photoconductivity of Conducting Polymers

TASK OBJECTIVE: To quantify the photophysics and conduction mechanisms in conducting and electro-optical polymers using photoconductivity and related methods. The parameters to be determined are energy gap, carrier sign, carrier lifetime, mobility, shape of the absorption edge, and quasi-particle energy levels.

SCIENTIST: Barney E. Taylor, Ph.D.

DESCRIPTION OF WORK:

The 6FPBO family of polymers are viable contenders for future commercialization as blue-emitting electroluminescent devices. A thorough understanding of the photophysics of the 6FPBO devices is needed before the commercialization can commence. The photoconductivity of two derivatives of 6FPBO (6FPBO-OD and 6FPBO-COPY) was measured in several different experiments. The goal of the experiments was to compare and contrast the two materials and to compare the 6FBPO data with that of other polymeric systems in an effort to understand the photophysics of these materials by means of photoconductivity (PC).

The photoconductivity of devices constructed of 6FPBO was measured as a function of applied bias, chopping frequency, and probe beam intensity. Bleaching studies that made use of a second, continuous beam of light were also performed on the samples. A relaxation of the PC was observed for 6FPBO photoconductivity samples. A study to compare the PC response on a large number of devices was also performed to obtain a baseline for the processing yield for the devices.

Although some work on the system is yet to be done, a heuristic model that describes much of the bias, bleaching and relaxation phenomena is presented.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 126, Photoconductivity Studies of the Non-Conjugated Polymer 6FPBO.

TASK: 156

TASK TITLE: Theoretical Prediction of Two Photon Properties of Organic Molecules

TASK OBJECTIVE: To use advanced quantum mechanical methods to predict Two Photon (TP) properties of selected organic molecules.

SCIENTIST: Guru P. Das, Ph.D.

DESCRIPTION OF WORK:

An ab initio formulation for calculating solvent effects for organic molecules are presented. The solvent is treated as a continuum with the cavity determined ab initio as a surface enclosing the solute molecule which represents the minima of the interaction potential as it approaches the solute molecule radially from various directions. During such radial approaches the charge environments both for the solute as well as the solvent are kept frozen. The electrostatic part of the interactionpotential is based on ab initio diatomic calculations on various pairs of atoms with frozen asymptotic charge densities. The polarization part is built in terms of ab initio localized polarizabilities of the constituent atoms of the solvent. The reaction field contribution from the solvent is evaluated by solving numerically an integral-equation analog of the Poisson equation at dense grid of points on the cavity. The method is demonstrated by application to the p-nitroaniline

in various solvents. The solvated excitation energies are calculated and compared with experiment. We also compute the solvated polarizabilities and second order transition moments.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 153, AN AB INITIO MODEL FOR SOLVENT EFFECTS IN ORGANIC MOLECULES

TASK: 157

TASK TITLE: Theoretical Prediction of Polymer Electronic Properties

TASK OBJECTIVE: To use advanced quantum mechanical methods to predict electronic structures and properties of selected organic molecules and polymers of interest for potential electrical and electronic applications.

SCIENTIST: Xiaofeng Duan, Ph.D.

DESCRIPTION OF WORK:

Symmetric ground state polymers incorporating squaric acid moieties in the polymer backbone are of interest as low band gap materials. These polymers are squarylium dyes and are known for their narrow and intense absorption bands in solution with large molar extinction coefficients. Extensive charge delocalization along the backbone of the polymers gives these materials semiconductive and photoconductive characteristics of interest for electrophotography, nonlinear optics, solar energy conversion and optical recording media.

This work focused on 1,2-phenylamino-squarine polymers having either aromatic or quinoidal bonding. The geometrics, ground and first excited state electronic structures for oligomers up to 6 repeat unit were investigated. The polymer structures and band gaps were extrapolated from the oligomer properties. Semi-empirical and ab initio SCF method were used to characterize the polymer and electronic structures. The CIS method was employed to calculate the excitation energies between ground singlet state and ground triplet state for a series of oligomers and the band gaps of either aromatic or quinoidal polymers were then extrapolated. The quinoidal polymer is highly polarizable with dipole moment per unit cell of 6.95 D while the aromatic

polymer has a dipole moment per unit of 2.47 D. In the ground electronic state, the two configurations have almost same stabilities, the difference of energy per unit cell is less than 0.7 kcal/mol. Both types of polymers show narrow band gaps which are close to 1.0 eV. The reduction from the quinoidal bonding polymer to the aromatic bonding dianion of the polymer is also studied in the work.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 151, Theoretical Investigation of Electronic Structures and Optical Band Gaps for 1,2-Phenylamino Squaraine Polymers

TASK: 158

TASK TITLE: Environmental Effects in Fretting Fatigue

TASK OBJECTIVE: To evaluate the role of environment in the development of fretting fatigue damage in titanium under high cycle fatigue conditions.

SCIENTIST: Mitsuo Niinomi

DESCRIPTION OF WORK:

The fretting fatigue tests of Ti-6Al4V were carried out using Cu-Ni plasma spray coated and as-received pads. The coated and as-received pads were then used repeatedly for the fretting fatigue tests in order to identify the endurance of the pads. The characterization of pads before and after testing, and tested specimens were carried out to investigate the mechanism of fretting fatigue of Ti-6Al-4V when using the Cu-Ni plasma spray coated pad.

Cu-Ni plasma spray coated layer is a single phase of solid solution. The fretting fatigue life of Ti-6Al-4V is prolonged by Cu-Ni plasma spray coating on the pads. The fretting fatigue strength of Ti-6Al-4V decreases with repeated time of test when the Cu-Ni plasma spray coated pads are repeatedly used. The opposite trend is however observed when the as-received pads are repeatedly used. The surface of Cu-Ni plasma coated pads is smoother after testing than before testing. The surface of as-received pads is however a little rougher after testing than berfore testing. The

transformed microstructure is observed on the specimen surface when the as-received pads are used. The small cracking is observed in the transformed microstructure.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 149, Effect of Cu-Ni Plasma Spray Coating on Fretting Fatigue Characteristics of Ti-6Al-4V Under Flat-on-Flat Contact

TASK: 159

This task was canceled.

TASK: 160

TASK TITLE: Modeling of Ultrasonic Inspection Techniques

TASK OBJECTIVE: To develop and validate models which support current in-house efforts to develop Picosecond Laser Based Ultrasound System (PLUS) techniques to characterize thincoatings, ultrasonic techniques to characterize anomalous microstructures in titanium, and ultrasonic techniques for characterizing incipient High Cycle Fatigue (HCF).

SCIENTIST: Waled Hassan

DESCRIPTION OF WORK:

This report summarizes some theoretical and experimental efforts directed towards understanding the properties and potential of some non-destructive materials characterization techniques in different configurations. It consists of four different parts. In part 1, a simplified formulation for the stresses and displacements in a Rayleigh wave is presented. It is shown that the identical amplitude ratio between the normal and transverse displacement components, the shear and normal stress components, and the vector and scalar potentials, is a direct result of the requirement that just below the surface even the oscillating power be parallel to the surface. In part II, we present an experimental verification of the opposite effect of fluid loading on the velocity of dilatational waves in thin plates and rods. It is shown that fluid loading increases the velocity of the dilatational wave in a thin plate but decreases it in a thin rod. In spite of the inherent difficulties

involved in these measurements, the presented experimental results provide unequivocal verification of the theoretical predictions.

In part III, theoretical and experimental investigations of the lateral resolution of eddy current imaging are conducted. Our results demonstrate that eddy current microscopy can be enhanced via a high-resolution, small diameter probe-coil which delivers a unique materials characterization tool well suited for the evaluation of Ti alloys. In part IV, the grain noise in interferometric detection of ultrasonic waves is experimentally investigated. It is shown that the incoherent grain noise significantly increases as the illuminated spot size decreases. Above the acoustic wavelength this is mainly due to the increasing sensitivity of the receiver to propagating scattered waves generated in the interior of the specimen. Below the acoustic wavelength, the further increasing material noise is mainly due to evanescent vibrations caused by nearby scatters.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 143, Experimental and Theoretical Investigations of some nondestructive materials characterization techniques in different configurations

TASK: 161

TASK TITLE: Microstructure-texture Relationships for Hot Working of Titanium Alloys

TASK OBJECTIVE: To establish the interrelation of microstructure and texture formation during thermomechanical processing of titanium alloys.

SCIENTIST: Thomas Bieler, Ph.D.

DESCRIPTION OF WORK:

The work accomplished is divided into the following four sections: Macro texture measurement of rolled specimens, Taylor modeling of large strain deformation in Ti-6Al-4V, microtexture (OIM) measurements of several specimens, and reverse beta transformation analysis of OIM data. The range of specimens and processing history examined included rolling, upset forging, equal channel angle extrusion, and laser deposition, and relevant microstructure included a batch annealed controlled cooling, that provided a colonied microstructure and a water quench from

the beta phase field that caused an acicular microstructure. Originally, plans were made to do partial extrusions in a stream line die to obtain a gradient of deformation in a tensile strain setting. FEM calculations were made to support this, and specimens were heat treated for this, but the specimens were not extruded in preference for other priorities.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 185, Microstructure-Texture Relationships for Hot Working of Titanium Alloys.

TASK: 162

TASK TITLE: Process Model Development for use with Discrete Event Optimization Techniques

TASK OBJECTIVE: The objective of this task is to significantly improve manufacturing processes with respect to product quality (material properties and reproducibility/robustness of the process), manufacturing costs (fewer processing steps are usually cheaper), and delivery time (improved response to customers schedule). The overall research objective is to establish a systematic methodology for accurately modeling and significantly improving manufacturing systems and their subsystems.

SCIENTIST: Jay Gunasekera, Ph.D. , STI, Inc., Greshan Fernando, STI, Inc., and Vipul Ranatunga, B.Sc., Ohio University

DESCRIPTION OF WORK:

This task is aimed at basic research for significantly improving manufacturing processes with respect to product quality (material property and reproducibility/robustness of the process), manufacturing costs (fewer processing steps are usually cheaper), and delivery time (improved response to customers schedule). The overall research objective is to establish a systematic methodology for accurately modeling and significantly improving manufacturing systems and their sub systems.

In this report, an Upper Bound Elemental Technique (UBET) has been developed as an analysis tool for modeling of forging of axisymmetric turbine rotors. The model divides the deformation zone into a number of upper bound elements for the analysis of energy dissipation due to internal plastic energy, friction, shear, and predicts an upper bound value for the total die load. The developed UBET model predicts the maximum allowable flash height in order to reach the die-fill in closed-die forging operations.

This project report presents an extensive comparison of the results obtained from Upper Bound Elemental Techniques, Slab Method, and Finite Element Methods (FEM) for the forging of an axisymmetric turbine rotor.

Part II of this report contains an Analytical Model for Electrochemical Machining (ECM) of an Axisymmetric Disk. In this ECM process modeling effort, three different processes has been considered. These processes are, Electrochemical process, which governs the mechanism of metal removal, Dynamics of the ECM process, and Electrolyte flow process inside the electrode gap. Results of this ECM model has been validated with available experimental data, and are found to be in good agreement.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 150, Process Model Development for Use With Discrete Event Systems Techniques.

TASK: 163

TASK TITLE: Multiaxial Fatigue Life Prediction

TASK OBJECTIVE: To develop a framework for determining the fatigue limit of metallic materials subjected to multiaxial fatigue states.

SCIENTIST: Alan R. Kallmeyer, Ph.D.

DESCRIPTION OF WORK:

An overview of the current state-of-the-art in multiaxial fatigue life prediction methodologies for metals is presented in this report, with an emphasis on crack initiation models. Multiaxial fatigue damage models were classified into three categories: (1) equivalent stress or strain models, (2) work or energy based models, and (3) critical plane models. The advantages and disadvantages of each type of model were compared and contrasted. Although equivalent stress or strain models have retained popularity due to widespread recognition and ease of use, the critical plane models have gained popularity because they are based on physical interpretations of fatigue crack initiation and they have shown good correlation with experimental data. The critical plane models appeared to be the most promising models for multiaxial fatigue crack initiation. However, no single model has gained widespread acceptance within the fatigue community.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 115, Multiaxial Fatigue Life Prediction Models: A Review.

TASK: 164

TASK TITLE: NDE Data Analysis

TASK OBJECTIVE: Optmize the extraction of significant information from noisy NDE image data using advanced mathematical techniques.

SCIENTIST: George N. Frantziskonis, Ph.D.

DESCRIPTION OF WORK:

Wavelet analysis has been used to rationalize information at various scales in several branches of science, including particle physics, biology, electrical engineering, fluid mechanics, and medicine. However, this powerful technique has not been applied to characterizing structures of materials, fretting damage for the present case, even though many critical questions could be addressed. In particular, the following unsolved problems were considered in this paper:

(a) The first problem dealt with the quantitative characterization of fretted surfaces in a Ti alloy. This was investigated by analyzing profilometric digital images of fretting surfaces obtained at a range of magnifications. Wavelet analysis of the data was able to identify, by examining the wavelet coefficients, dominant length scales as those regions in the scale-space where the energy of the wavelet transform and/or peaks of local concentration dominate. For the range of magnifications examined, i.e. from 1.25x to 100x, the ~20x magnification was identified as the one with the most useful information.

(b) An alternative procedure was employed for the second use of wavelets which dealt with the non-uniformity of the contact regions. Recent theoretical work has shown that during contact with partial slip, the morphology of the partially slipping regions does not change. Wavelet analysis was employed to identify those regions, which resulted in the "pattern" of the fretted surface morphology.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 120, Wavelet Analysis of Fretting Experimental Data.

TASK: 165

TASK TITLE: Microstructural Characterization of Coatings and Fibers for Ceramic-Matrix Composites

TASK OBJECTIVE: The objective of this task is the characterization of novel coatings applied to ceramic fibers. Overall coating uniformity, as well as composition, morphology, and crystallography are to be determined in support of the ceramic fiber coating effort being conducted as part of the development of an oxidation-resistant fiber-matrix interface for ceramic-matrix composites.

SCIENTIST: Yolande Berta

DESCRIPTION OF WORK:

Previously prepared samples of heat-treated 3M Nextel 720 fibers were examined by transmission electron microscopy. The images of its two distinct phases, alumina and mullite, were recorded on film for three heat treatment regimes (1350°C, 1400°C and 1450°C) and times ranging from 20 minutes to 300 hours. Three more heat treatment regimes remain, for analysis by the ceramics group. The grain sizes of the two phases were measured in the long and short dimensions, the data plotted following the Arrhenius equation, and from the slope of the plot, the mechanism of grain growth was deduced.

Two ceramic matrix mini-composites and a control, using the Nextel 720 fiber, were prepared for microscopy. Of the two ceramic matrix mini-composites, one was processed in air, and the other in argon. The "air" sample showed the attachment of the matrix to the fiber. The "argon" sample requires further work.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 119, Grain Growth in 3M Nextel 720 Fiber; Phases in a Ceramic Matrix Mini-Composite.

TASK: 166

This task was canceled.

TASK: 167

TASK TITLE: An *In-Situ* Tracer Method for Establishing the Presence and Predicting the Activity of Heavy Metal-Reducing Microbes in the Subsurface

TASK OBJECTIVE: The objective of this work is to develop *in-situ* tracer method for detecting the presence and quantifying the activity of the microbial communities associated with the reduction of heavy metals in the subsurface. The end goal being a field-based tool using chemical tracers interacting with metal-reducing microbes in the subsurface and the concomitant behavior of the dissolved heavy metals to obtain estimates of the distribution and activity of these bacteria.

SCIENTIST: Charles Somerville, Ph.D. and Steven Foster

DESCRIPTION OF WORK:

The objective of this study was to contribute to the design of a field tool for detecting the presence of soil microorganisms and estimating their metabolic potential in-situ. Microbiological studies were conducted in three phases. First, bacterial isolates were recovered from two sites; one previously exposed to heavy metals and one with no known exposure history. The isolates were then tested for their ability to metabolize 101 chemical substrates. Finally, compounds that were frequently metabolized by the soil isolates were tested in batch growth experiments. Bacterial isolates from the two sites had very distinct metabolic properties. The differences suggest that carefully chosen chemical tracers can discriminate between exposed and non-exposed soil communities. Furthermore, specific microbial populations can be studied within the larger community by matching the target organisms with specific metabolic profiles. In batch experiments, microbial growth lagged for at least six hours after addition of substrate. Such lag times are sufficiently long to allow the addition of a pulse of biodegradable substrate to the subsurface without altering the size of the microbial community. The data support the development of the proposed field tool, but further work is required to verify that abiotic effects can be differentiated from microbe-specific partitioning.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 148, An IN-SITU Tracer Method for Establishing the Presence and Predicting the activity of heavy metal-reducing microbes in the subsurface

TASK: 168

TASK TITLE: Computer Model of Unmanned Systems for Active Range Clearance and UXO Remediation

TASK OBJECTIVE: The objective of this task shall be to update and continue development.

SCIENTIST: Rita Gregory, Ph.D.

DESCRIPTION OF WORK:

This report summarizes investigation for international partnerships and technology transfer with various European Countries. AFRL (formerly Wright Laboratory) formalized an Education Partnership Agreement in 1997. Additional goals for this summer research were to improve and/or enhance the Remedial Action Cost Engineer and Requirements (RACER) System to support the Cost Engineering studies for the AFRL/MLQC Automation and Robotic Program. The technologies cover a wide variety of interests in the fields of Civil and Environmental Engineering, with particular interest in automation and robotics, construction engineering, cost engineering and management. In addition, a parallel study included an elementary school curriculum developer to help design technology integration in K-12 curricula in an effort to attract and prepare more U.S. students in engineering and sciences. The work was conducted by means of visits, discussions with technical leaders and managers, and supporting documentation reviews when documents were made available. Visits were conducted during the summer 1998. Organizations contributing to and interested in this effort include the Air Force Research Laboratory, Air Base Technology Branch, Georgia Institute of Technology (GA TECH), Georgia Tech Research Corporation, Georgia Tech Foundation, and the National Science Foundation.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 123, Opportunities for International Partnerships and Technology Transfer to Support RACER Development.

TASK: 169

TASK TITLE: AC Transport Studies of SiC and Related Materials

TASK OBJECTIVE: The objective of this task is to develop experimental techniques for the measurement of transport properties of low mobility semiconductors such as silicon carbide and gallium nitride. The techniques must be suitable for operation at temperatures up to 700°C.

SCIENTIST: Richard Newrock, Ph.D.

DESCRIPTION OF WORK:

This project attempted to create a very sensitive phase sensitive detection system for accurately determining the Hall and longitudinal resistivity of wide-band gap semiconductors. These parameters can yield the carrier density, carrier lifetime, and mobility over a wide range of temperatures.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 147, NDE Data Analysis.

TASK: 170

TASK TITLE: Chromophore/Gel Systems for Optical Limiters

TASK OBJECTIVE: To: 1) continue to expand the range of optical quality (visible through near infrared) for coating materials deposited in MLPJ's plasma enhanced chemical vapor deposition chamber for the protection of personnel from laser radiation, and 2) develop new techniques to synthesize, process, and characterize gel and elastic polymer-based host-optical limiting materials for sensor protection against high intensity laser irradiation.

SCIENTIST: Hao Jiang, Ph.D.

DESCRIPTION OF WORK:

Two types of chitosan hydrogel systems have been prepared which have a laser damage threshold (LDT) up to 35 times higher than commercial PMMA bulk materials. For these samples, the LDT increases with increasing water content. The mechanism of laser damage and the contribution of water to their high laser damage resistance have been examined. DSC measurements indicate water within the hydrogels exist in various states, each with different laser damage resistance properties. These various states play a key role in determining the LDT by controlling the dissipation of laser energy and providing a mechanism for self-healing. This preliminary research shows that polymer hydrogels have potential for high power laser applications since they combine good mechanical integrity due to the polymer frame and good energy dissipation and healing characteristics due to the molecular mobility of water. These two

traits allow for bulk shape retaining films with high laser damage thresholds and potential reversibility in damage processes.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 139, Chitosan-based Hydrogels: A New Polymer-based System with Excellent Laser Damage Threshold Properties.

TASK: 171

TASK TITLE: Life Prediction Methods for Small-cracks in Gamma TiAl Alloys

TASK OBJECTIVE: To develop an understanding of the mechanics and physics of the development and growth of small fatigue cracks in gamma titanium aluminide alloys.

SCIENTIST: K.S. Ravichandran, Ph.D.

DESCRIPTION OF WORK:

Surface cracks from which fatigue failures occurred in Gamma TiAl alloys, showed unusual shape characteristics which required a detailed analysis of stress intensity factor variations along the crack front. This research documents the development of an approach to determine the stress intensity factors for any arbitrary shaped crack. For this purpose, the displacement field solution, proposed by Fabrikant was modified. A comparison of stress intensity factor calculated by this approach, was compared with the exact and numerical solutions available in literature. It has been found that for elliptical cracks with aspect ratios in the range of $0.5 \leq a/c \leq 2.0$, the present approach yielded results which were within about 10% of the exact solution. The approach was used to calculate the stress intensity factors for irregularly shaped flaws in fatigued gamma TiAl specimens.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 118, Stress Intensity Factor Calculations for Irregular Cracks in Gamma TiAl Alloys

TASK: 172

TASK TITLE: Synthesis and Characterization of Nonlinear Absorber

TASK OBJECTIVE: To assist the in-house synthesis group in synthesis and spectroscopic characterization of porphyrins and other compounds.

SCIENTIST: Morton Raban, Ph.D.

DESCRIPTION OF WORK:

The work performed consisted of two parts: a) preparation and presentation of a tutorial (short course) on modern methods for NMR spectroscopy and b) measurement and interpretation of NMR spectra of porphyrins and other molecules. The tutorial consisted of lectures given twice a week for a period of 6 weeks and a research seminar given at the end of the period. The subjects covered included: Introduction to Structure Determination using H and C NMR, Fourior Transformation (FT-NMR) Spectroscopy, and 2-D NMR Spectroscopy. The NMR spectra taken included numerous porphyrins and other molecules synthesized at MLPJ. These spectra helped to characterize the compounds and support structural assignments. One compound, octaethyltetraphenylporphyrin (OETPP), showed unusual spectroscopic behavior and was selected for more extensive examination including a variable temperature study which formed the basis for this report.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 117, Nuclear Magnetic Resonance Spectroscopy of Porphyrins and Other Compounds.

TASK: 173

TASK TITLE: Threshold Crack Growth Behavior in Titanium Alloys

TASK OBJECTIVE: To evaluate the effects of crack geometry and crack length on the threshold and near-threshold crack growth behavior in titanium alloys under

combined low cycle and high cycle fatigue. To develop mechanistic models for predicting the crack growth threshold in titanium alloys as a function of load history and stress state near the crack tip.

SCIENTIST: Weiju Ren

DESCRIPTION OF WORK:

Two of the major causes for high cycle fatigue problems in airplane gas turbines have been planned for investigation, which is divided into two projects: 1) Interaction of low cycle fatigue and/or creep effects with subsequent high cycle fatigue, and 2) Fretting damage and coating effects on high cycle fatigue. Specimens have been designed and are being machined in workshops. Mechanical testing, microstructural characterization and finite element analysis preparations, literature review and DOD clearance check are underway. The investigation will provide information for some fundamental understanding of high cycle fatigue and related mechanisms for the National High Cycle Program of the U.S. Air Force.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 167, Threshold Crack Growth Behavior in Titanium Alloys.

TASK: 174

TASK TITLE: Surface Chemistry and Performance of Spacecraft Lubricants

TASK OBJECTIVE: To determine the nature of friction and wear of spacecraft materials from a surface chemistry and performance perspective.

SCIENTIST: Jeffrey N. Cutler, Ph.D.

DESCRIPTION OF WORK:

New material systems hold promise for increased reliability, lower torque noise and longer lifetimes in high-speed bearings for spacecraft. These new materials include stable, low volatility fluids in conjunction with alternative solid surfaces: either new bulk materials or surface

modifications effected by treatments or coatings. In order to study these materials in a simulated space environment, a series of vacuum testers have been developed which allow performance testing in the 10-7 Pa regime. A number of surfaces (e.g., Si3N4, TiCN, TiN, etc.) in the presence of multialkylated cyclopentane were evaluated. By applying various ex situ spectroscopic techniques (e.g., GAM-FTIR, XPS, XANES) and surface energy measurements, it has been possible to understand the tribochemistry and associated wear. These phenomena are then related to the improved performance of the tribosystem. This presentation will focus on the chemistry produced in vacuum by the fluid and its interactions with various surface coatings.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 136, Surface Chemistry of New Lubrication Systems for high-speed spacecraft devices

TASK: 175

TASK TITLE: Development of Antistatic Repair Coating

TASK OBJECTIVE: The objective of this task is to develop an antistatic repair coating that provides long-term conductivity and ease of repair for future aircraft coating systems.

SCIENTIST: Thomas J. Fabish, Ph.D.

DESCRIPTION OF WORK:

We describe the development of an Advanced Battle Damage Repair (ABDR) coating having the attributes of high electronic conductance, excellent adhesion to a variety of substrates, good radiation and fluid resistance, respectable corrosion resistance, and application by a variety of field-suitable hand and spray methods. The program deliverable is specifications for two screen tested systems for scale-up to volumes appropriate for field evaluation: a viscous, thixotropic system optimized for application by an assortment of hand tools and a lower viscosity but faster HVLP (High Volume Low Pressure) sprayable system. Repairs of large area 'race track' damage patterns placed in the current four layer stack on aluminum and graphite fiber composite substrates show the recommended ABDR systems to be versatile and robust. A credible repair can be

accomplished in a single draw down with dry to tape of two hours. Other hand and spray methods are equally effective but some may require two coats and others a finishing sanding operation to achieve target surface roughness. Effort is devoted to establishing a basis for the observed film properties in materials structure and film morphology, revealing the dominant mechanisms of electronic transport and mechanical properties enhancement, and in the design of critical experiments.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 172, Development of Antistatic Repair Coating.

TASK: 176

TASK TITLE: Flow Instability During Equal Channel Angular Extrusion (ECAE)

TASK OBJECTIVE: To establish the effect of processing parameters on flow uniformity during hot ECAE of Ti-6Al-4V and nickel alloy 718.

SCIENTIST: David P. DeLo, Ph.D.

DESCRIPTION OF WORK:

Deformation behavior during Equal Channel Angular Extrusion (ECAE) was examined experimentally and the results used to improve the ECAE process for difficult-to-work materials. An initial degree of upset deformation preceding ECAE was found to dramatically decrease the nonunifromities observed in similar material processed by conventional ECAE. Characterization of the microstructural evolution and texture development during ECAE continues.

The results of discrete element simulations of Ti-6Al-4V and Ti-24Al-11Nb powder consolidation processes were compared with experimental observations and analytical model predictions. Differences between the simulation results, experimental measurements, and analytical model predictions were attributed in part to differences in the mechanisms represented in the simulation and analytical models when compared to the experimental observations. The possibility

of numerical flaws in the model was also noted. The predictions from a hybrid continuum-micromechanical powder consolidation model were compared with the results of hot isostatic pressing and hot triaxial compression experiments. The hybrid model was found to predict a slower densification rate than was observed experimentally but the predictions were much closer to the observations than were the predictions from a classical micromechanical model. Further compression experiments were performed on porous compacts to obtain more accurate material property data for the model. The refined material data improved the model performance. Remaining discrepancies between the model predictions and experimental observations were attributed to mechanisms that are not completely represented in the model or in the measured material properties for the model.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 152, Metallurgy and Advanced Metallic Materials: Equal Channel Angular Extrusion of Ti-6Al-4V and Discrete Eleement Modeling of Titanium Alloy Consolidation.

TASK: 177

TASK TITLE: Mechanical Behavior and Toughness of Fibrous Monolithic Ceramics

TASK OBJECTIVE: To develop an understanding of the complicated fracture behavior in highly textured ceramics.

SCIENTIST: James M. Staehler, Ph.D.

DESCRIPTION OF WORK:

This investigation was intended to provide a good understanding of the room and high temperature mechanical behavior of single filament Si3N4/BN fibrous monoliths. Mechanical behavior included monotonic tension, tensile creep rupture, tension-tension fatigue, as well as notch sensitivity. Three different architectures were considered but to different extents. They were a 0°/90° symmetric cross-ply, a 90°/0°/45°/-45° quasi-isotropic, and a random chopped material with 40:1 aspect ratio chopped filaments. The quasi-isotropic material received the most attention. It also had some of the best material properties of the three architectures but did exhibit notch

sensitivity. The cross-ply and random chopped lay-ups were comparable in room temperature tension. Their notch sensitivity seemed to be less significant compared to the quasi-isotropic material. From 23°C to 1000°C tensile strengths in the quasi-isotropic material drop by about 30-35%. In the cross-ply material the drop was a less dramatic 20-25%. Creep rupture and fatigue (1 Hz) tests at 1000°C and 1100°C were performed on the QI material using a 50 hour run-out condition. The creep rupture limits were estimated to be about 65 MPa and 35 MPa at 1000°C and 1100°C, respectively. Measurable creep strains were reduced at both 1000°C and 1100°C. In fatigue the limits were 75 MPa and 55 MPa at 1000°C and 1100°C, respectively. There was some indication of size dependence, more-so in the cross-ply and random chopped architectures. In addition, there did appear to be a location dependence to the tensile properties of specimens prepared from some of the hot pressed plates. There was also an indication of significant plate-to-plate variability. A few unidirectional specimens were also evaluated in tension but tended to slip in the grips and were prone to crushing when gripping pressures were raised.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 171, Mechanical Characterization and Notch Sensitivity of Cross-ply, Quasi-Isotropic, and Random-Chopped $Si_3N_4$/BN Single Filament Fibrous Monoliths

TASK: 178

TASK TITLE: The Synthesis of Water Soluble Chromophores Which Exhibit Strong 2 Photon Generated Upconverted Emission

TASK OBJECTIVE: To synthesize water soluble organic molecules which when irradiated with near infrared light (800nm) undergo 2-photon absorption and/or excited state absorption and strong upconverted fluorescence emission in the visible.

SCIENTIST: Ram Kannan, Ph.D.

DESCRIPTION OF WORK:

Syntheses of seven new fluorene derived, two photon absorbing chromophores are reported. All the chromophores possess, an electron donor diphenyl amino group and electron acceptors, benzothiazole, benzimidazole and triazine. Two chromophores are symmetrical and others are non-symmetrical. One of the chromophores is functionalized with two allyl groups for sol-gel applications. Efforts to produce amine and hydroxyl functionalized chromophores are also given. All the chromophores are designed to respond to 800 nm irradiation.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 180, Synthesis of Functional Derivatives of Two Photon Absorbing Dyes.

TASK: 179

TASK TITLE: Molecular Modeling Methodology Applied Toward Paint IR Signatures

TASK OBJECTIVE: To evaluate the validity of applying modern modeling techniques to the problem of predicting paint IR signatures.

SCIENTIST: Xiaofeng Duan, Ph.D.

DESCRIPTION OF WORK:

In this project, various modern molecular modeling techniques were applied to the problem of predicting paint signatures in the thermal infrared. The quantum mechanics methods at different levels of theory were employed to predict sample material thermal signatures based on known molecular structures and compare them to experimental IR spectra. Molecular Mechanics and Semi-Empirical method were used to obtain the initial geometries of the molecules, and then the ab initio as well as Density Functional Theory methods were used to reoptimize the structures and then to carry out the normal mode vibrational frequency calculations. In some cases a post SCF calculation, such as MP2 method, was carried out for both geometry optimization and vibrational frequency calculations. The Self Consistent Reaction Field (SCRF) calculations with Onsager's

spherical solvent reaction model were carried out to examine the effects of different solvents on binder molecules.

A "C" program was written to convert the vibrational frequencies and IR intensities to a continuous realistic look spectrum. The structures and IR spectra of the binder molecules including Methyl-Acrylate, Aromatic Epoxy and Cordura E with four different R group combinations were calculated and compared with their experimental IR spectra. The solvents effects to the IR spectra of some of these binder molecules were investigated. The IR spectra for two organic dye molecules, Para Red and Toluidine Red, and one organometallic pigment, Pigment Blue 15, was examined.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 188, Computer Prediction of Infrared Paint Signatures.

TASK: 180

TASK TITLE: Characterization, Imaging, Sensor, and Simulation Techniques of Thin Film Growth, Growth Processing, and Analysis.

TASK OBJECTIVE: The objective of this task is to continue to develop data collection and manipulation capabilities for implementation of characterization, imaging, sensor, and simulation techniques of thin film growth, growth processing, and analysis.

SCIENTIST: Donald R. Thomas, M.S.

DESCRIPTION OF WORK:

A number of personal computer-based solutions are presented to:

- Aid in the successful growth of epitaxy thin films.
- Nanoscopically scribe patterns in semiconductor materials in order to create devices such as quantum dots, diffraction gratings, and MEMs.

- Control a semiconductor wafer bonding process.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 183, Personal Computer Solutions to Aid in Thin Film Growth and Semiconductor Wafer Bonding.

TASK: 181

TASK TITLE: Molecular Modeling of Polysiloxanes and Silsequioxanes

TASK OBJECTIVE: The objective of this task is to study, using modern molecular modeling techniques, the behavior of (1) polysiloxanes having side-chain liquid crystalline character, and (2) silsequioxanes having various pendants and molecular architectures.

SCIENTIST: Rishikesh Bharadwaj, Ph.D.

DESCRIPTION OF WORK:

Atomistic molecular dynamics simulations have been used to delineate the effect of introducing polyhedral oligomeric silsesquioxane (POSS) moieties substituted by cyclopentyl (C5POSS) and cyclohexyl (C6POSS) rings as pendant groups on polynorbornene. Calculated volume-termperature behavior and X-ray scattering profiles matched well with experimental results. Most importantly, the effects of incorporating the POSS moieties into the polymer have been identified via simulations. These were judged on the basis of the increase in the glass transition temperature, retardation of the chain dynamics and improvements in the calculated elastic tensile, bulk and shear moduli of the POSS containing polymers compared to the norbornene homopolymer. The most important conclusion from the study is that aggregation of the POSS moieties is not required for the beneficial effects to be realized. Indeed, the simulations show that there is no tendency for affregation to occur among the POSS moieties if they are well dispersed to begin with. It is reasoned that the chief source of reinforcement arises form the POSS moieties behaving as strong anchor points in the polymeric matrix.

Director configurations of liquid crystalline molecules packed in ellipsoidal domains have been investigated using mesoscale modeling techniques. Four different ellipsoidal shapes (sphere, oblate spheroid, prolate spheroid, and ellipsoid) were studied under homogeneous and homeotropic surface anchoring conditions. The model has been characterized by computing thermodynamic and structural properties as a function of ellipsoidal shape (prolate and oblate) and size. The director configuration in ellipsoids resulting from homeotropic and homogenous surface anchoring have been delineated. The effect of an external electric field applied at different orientations with respect to the major axis of the ellipsoid has been probed as a function of the magnitude of the field and ellipsoidal size and shape. The orientation of directors is most easily accomplished parallel and perpendicular to the major axis for the oblate and prolate spheroids respectively for homeotropic anchoring and along the bipolar symmetry axis for homogeneous anchoring. In domains with homeotropic surface anchoring, the oblate spheroid and elongated ellipsoid, and for homogeneous anchoring conditions, the prolate spheroid and elangated ellipsoid were found to be the most efficient geometries for PDLC applications.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 205, Molecular Modeling of Polysiloxanes and Silsequioxanes.

TASK: 182

TASK TITLE: Tribology of Quasicrystals

TASK OBJECTIVE: To characterize the friction and wear properties of quasicrystalline materials in different environments, and to characterize the chemistry and microstructure of quasicrystalline coatings and relate them to tribological properties.

SCIENTIST: Jeremy O'Neill, B.S.

DESCRIPTION OF WORK:

Several AlCuFeCr coatings, having a small range of compositions centered around $Al_{71.7}Cu_{5.0}Fe_{11.3}Cr_{12.0}$ (the microcrystalline approximant to the decagonal phase), were grown by magnetron sputtering. As-deposited, the coatings were amorphous. In order to induce crystallinity, they were annealed under argon gas or vacuum. This produced a surface oxide ranging in thickness from 7-100 nm, depending on the temperature and atmosphere. The sliding friction and wear of these coatings was analyzed as a function of composition and oxide thickness, as well as sliding partner. Against 440C stainless steel, a coating with composition $Al_{74.7}Cu_{5.0}Fe_{8.6}Cr_{11.6}$ had the lowest friction, 0.22, for over 2400 cycles. Against $Si_3N_4$, oxide thickness was the determining factor, as it appeared to provide wear resistance and lubrication.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 178, Characterization of Friction and Wear Properties of the MC3 Approximant to Decagonal Quasicrystalline Coatings in the AlCuFeCr System.

TASK: 183

TASK TITLE: Plasma Deposition of Low Friction Hard Coatings

TASK OBJECTIVE: To develop new tribological films, which have novel microstructures, to enable multiple tribological functionality. To investigate the use of carbides, nitrides, and diamond-like carbon (DLC) in these films for load carrying and wear resistance and solid lubricant materials to provide low friction in dry, moist, and UHV environments. To understand the evolution of microstructure through the characterization of plasma energy.

SCIENTIST: Jeremy O'Neill, B.S.

DESCRIPTION OF WORK:

Magnetron assisted pulsed laser deposition (MSPLD) technique was used to produce composite tribological coatings with low friction characteristics. The composite coatings were prepared within the W-C-S material system. Coatings were consisted of 1-2 nm WC and 5-10 nm

WS2 grains embedded in an amorphous DLC matrix. These WC/DLC/WS2 nanocomposites demonstrated low friction and wear in tests performed in high vacuum, dry nitrogen, and humid air. The coatings were also found to adapt to the test conditions, which resulted in; (i) crystallization and re-orientation of initially nanocrystalline and randomly oriented WS2 grains; (ii) graphitization of the initially amorphous DLC matrix; (iii) reversible regulation of the transfer film composition between WS2 and graphite with environmental cycling from dry to humid; and (iv) possible DLC/WS2 synergistic effects, providing friction reduction in oxidizing environments. Mechanical properties of these films (0.5μm) coatings could reversibly change with applied load and environment, providing the best wear protection. In particularly, a transition of mechanical response from hard and rigid to quasi plastic by grain boundary sliding at loads above the elastic limit was realized. At the same time the hardness of WC/DLC and TiC/DLC composites was maintained on a relevantly high levels of 27-32 GPa, while their scratch toughness was 4-5 fold above that of nanocrystalline carbides. The WC/DLC/WS2 composites survived millions of sliding cycles in vacuum and air under 500-1000 Mpa loading, and exhibited excellent friction recovery in humid dry environmental cycling. Their friction coefficients were about 0.1 in humid air, 0.03 in vacuum, and as low as 0.007 in dry nitrogen. The proposed self-adaptive concepts and their realization mechanisms dramatically increase wear resistant coating applicability, durability, and realiability.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 169, Plasma Deposition of Low Friction Hard Coatings.

TASK: 184

TASK TITLE: High Performance Coatings

TASK OBJECTIVE: Formulation of high performance organic coatings with the state-of-the-art commercially available raw materials and newly synthesized organic polymers. These coatings will be the bases for a fundamental study on degradation mechanisms.

SCIENTIST: George Pacinda

DESCRIPTION OF WORK:

The mission of the WUD-2 Task I Mechanisms of Coatings Degradation is to create revolutionary new coatings technology for Air Force applications using a basic research approach to coatings science. Research efforts have centered on both physical and chemical degradation studies, carried out on model formulated coatings of known commercial and chemical compositions. Our efforts have been to determine what structural changes in the coatings relate to both improved durability and improved cleanability.

Model formulated urethane coatings were prepared using commercially available materials and processed on Al-2024-T3 substrates. Baseline physical properties testing was performed (hardness, low temperature impact resistance, color, gloss, cleanability, etc.) prior to accelerated artificial weathering in both QUV-A (340 nm peak), QUV-B (313 nm peak), and Xenon Arc (Atlas Ci-35A) weatherometers.

The objective of this task was to aid in the development of an aircraft topcoat system with a focus on excellent long term outdoor weatherability, service durability, cleanability, and stain-resistance. The results of this work were intended to show the effect of different raw materials (polymer resins and extender pigments) and formulation parameters in obtaining a coating that meets the required specifications.

The use of High Irradiance QUV-A (1.35 W/m2) gives rapid, repeatable chalking and coating degradation, not only faster than standard QUV-A exposures, but also more realistic than standard QUV-B exposure. Chalking is much more pronounced.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 208, Mechanisms of Coatings Degradation in Durable/Cleanable Coatings.

TASK: 185

TASK TITLE: Surface Chemistry and Performance of Spacecraft Lubricants

TASK OBJECTIVE: To determine the nature of friction and wear of spacecraft materials from a surface chemistry and performance perspective.

SCIENTIST: Jeffrey N. Cutler, Ph.D.

DESCRIPTION OF WORK:

Multialkylated cyclopentane (MAC) and silahydrocarbon (SiHC) are primary candidates for future spacecraft applications due to their high viscosity and good viscosity-temperature profile, low vapor pressure and good lubricating properties. In this report, the friction, wear and associated tribochemistry of these fluids, both unformulated and formulated with 2% aryl phosphate ester (TPP), were investigated. A Plint reciprocating wear rig equipped with an environmental chamber that was filled with dry air or nitrogen was used to produce boundary lubrication conditions. The resulting specimens were examined by X-ray absorption near edge structure (XANES) spectroscopy in order to gain some understanding of how the base fluid and additive function.

Several relationships were discovered among friction, wear and tribochemistry within the wear scar. First, the wear rate in both unformulated and formulated fluids was higher in a dry nitrogen environment than in dry air. Second, when tested in air, unformulated silahydrocarbon acts as its own antiwear additive by decomposing to a silicon oxide glass within the wear track thereby eliminating additive issues such as solubility, evaporation and concentration effects. Third, the anitwear properties of silahydrocarbon oil are hindered by the presence of a phosphate additive. Both the oil and additive form an oxide glass within the wear track and compete for active growth sites. Fourth, the chain length of the polyphosphate glass formed in the wear track controls the antiwear performance of the film. The phosphate additive in multialkylated cyclopentane decomposed to a polyphosphate glass in both dry air to generate a good antiwear film (short to medium chain length polyphosphate) and nitrogen to form a poor antiwear film (long chain length polyphosphate).

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 181, Characterization of Surface Layers formed by "State of the Art" Lubricants and Additives for use in High-Speed Spacecraft Devices.

TASK: 186

TASK TITLE: Project Management/Administration

TASK OBJECTIVE: To provide for those project activities necessary to establish project task orders and overall contract management and administration.

SCIENTIST: Nagu Nagarajan

DESCRIPTION OF WORK:

The contributive research and development project required extensive management and administration activities that were not readily charged to a specific task. These activities fell into three general categories:

1. Those contract management administrative requirements to establish planning and control procedures that applied to the project as a whole. Examples are status reporting, project management meetings, and other general overall project reporting.

2. Those management activities required to establish each of the task assignments. These activities could not be charged to the task since the task was not yet approved during this phase.

3. Recording and reporting the performance and cost for the overall management and administrative activities.

This task provided project management/administration from 16 December 1998 through 22 December 1999.

TASK: 187

TASK TITLE: Heterointerface Formation during MBE Growth of Semiconductor Thin Films: Growth Modeling and Heterointerface Characterization

TASK OBJECTIVE: To develop and use computer models of MBE growth to determine the optimal growth conditions to obtain heterostructure materials with compositionally uniform layers and atomically flat interfaces.

SCIENTIST: Dr. Krishnamurthy Mahalingam

DESCRIPTION OF WORK:

A kinetic Monte Carlo model is developed to examine the influence of As/Ga flux ratio on the Ga desorption kinetics during molecular beam epitaxy of (100)-GaAs, based on data reported in desorption mass spectrometry experiments. A good match to experimental results is obtained when a mechanism involving desorption from a physisorbed state is included, in addition to desorption from a chemisorobed state. The results further reveal that the dependence of the Ga desorption energy on As/Ga flux ratio, observed in growth experiments, is explained in terms of the component due to desorption from the physisorbed state.

Transmission electron microscopy (TEM) studies were performed to investigate the use of compliant substrates for epitaxial growth of lattice-mismatched systems. The results indicate that the degree of twist bonding and thickness of the compliant layer are important parameters which control the dislocation density in the epitaxial layer. Preliminary results on the use of exit-plane wave functions for atomic scale compositional mapping of interfaces is also presented.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 175, Growth Modeling and Transmission Electron Microscopy Studies on III-V Compound Semiconductor Heterostructures Grown by Molecular Beam Epitaxy.

TASK: 188

TASK TITLE: Processing and Characterization of High-Performance Polymeric Materials for Space and Rocket Applications

TASK OBJECTIVE: To provide a fundamental understanding of the structure/property relationships that exist for high-performance polymeric materials identified

as leading candidates for use in rocket and space applications. The benefits from this study will be a more thorough understanding of the properties of specific thermoplastics which result from various modifications to the chemical structure of the materials and the ability thereby to tailor this class of materials for optimal performance.

SCIENTIST: Dr. Hong Guk Jeon

DESCRIPTION OF WORK:

Linear inorganic-organic hybrid polymers have received significant attention recently due, in part, to the potential for rational materials design and synthesis combining inorganic and polymeric properties. POSS macromers consist (as an example) of a well-defined cluster inorganic silica-like core (Si8O12) surrounded by eight organic corner groups (P1R7), only one being reactive for polymerization (P). Recently, norbornyl-POSS hybrid random copolymers possessing either cyclohexyl corner groups (CyPOSS) or cyclopentyl corner groups (CpPOSS) have been synthesized and characterized. Owing to the POSS-reinforcement of the parent polymer (polynorbornene), thermal stabilityand mechanical properties have been found to be enhanced by increasing the mole fraction of POSS macromers. More interestingly, the type of cycloalkyl group present in the POSS macromer affects the ordering of POSS macromers in polynorbornene, which likely causes the modification of physical properties. In order to further understand the structure-property relationships of these newly developed hybrid polymers , wide-angle x-ray scattering, transmission electron microscopy, and thernomechanical analysis have been performed on samples containing 50 wt% of the POSS macromer and have been mechanically drawn at temperature above their Tgs and then quenched. X-ray results show that the direction of POSS-POSS correlation is preferentially oriented along the draw axis, while orientation of polynorbornene chains along the draw axis is hindered (relative to pure polynorbornene) due to intermolecular POSS-POSS interactions. Shape memory properties of such drawn samples were also explored by measuring recovered strain while heating above the glass transition temperature using thermomechanical analysis. Additionally, TEM micrographs of various planes in the drawn and undrawn samples suggest possible arrangements of CpPOSS or CyPOSS macromers. Morphological changes which depend on the POSS corner group which, in turn, affects the shape recovery characteristics, such as recovery amplitude, rate, and strength have been investigated.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 174, Characterization of Microstructure and Strain Recovery of Poly(norbornyl-POSS) Copolymers.

TASK: 189

TASK TITLE: Evaluation of High Performance Polymeric Materials With Nuclear Magnetic Resonance (NMR) Spectroscopy

TASK OBJECTIVE: The objective of this research is to utilize NMR Spectroscopic techniques in the evaluation of high performance polymeric and composite materials.

SCIENTIST: Dr. Brett Cowans

DESCRIPTION OF WORK:

This research has involved the troubleshooting, modification, and repair of a Tecmag NMR spectrometer. The spectrometer provides essential information to the Materials Directorate for the investigation of cure and hydrolysis mechanisms in high temperature poly(imide) materials. Improvements and modifications to the spectrometer are discussed as well as the troubleshooting of several problems. These modifications have provided significant improvement in the spectrometer's performance and have directly improved the data obtained in the study of high temperature polyimide materials. Recommendations are made for routine calibration and operation.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 193, Solid-State Nuclear Magnetic Resonance Spectroscopy of Polymeric Materials.

TASK: 190

TASK TITLE: Second Layer Crack Detection in Aluminum Aircraft Structures

TASK OBJECTIVE: To investigate the potential of Remote Field eddy current inspection (RFES) to dectec cracks in the second layer of aluminum bolted aircraft structures.

SCIENTIST: Dr. Yushi San

DESCRIPTION OF WORK:

A high resolution experimental capability has been developed to map the phase and magnitude of ultrasonic waves transmitted in a solid. The advancement presented in this report is provided by laser detection of the ultrasonic energy over a microscopic aperture of approximately 50 mm and a special high-sensitivity phase mapping configuration. The system is built around a computer controlled scanner and a confocal Fabry-Perot interferometer, which uses a diode pumped Nd:YAG laser as a light source. Wave propagation in the axial and radial directions of a 2.5"-diameter bar of highly textured Ti-6Al-4V was investigated in this study. The work was motivated by the observation of unusually high attenuation in the axial direction of the as-received bar, which was thought to be associated with phase distortion rather than intrinsic attenuation loss. The current phase mapping results, using a focused laser spot, show relatively high wavefront distortion and more nonuniform distribution of the transmitted energy in the axial direction. The contribution to attenuation associated with phase cancellation loss was also investigated. These measurements show the laser detected attenuation to be substantially lower than the piezoelectrically measured coherent attenuation. However, even the relatively phase-insensitive focused laser detection clearly indicates that the attenuation is stronger in the axial direction.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 165, Phase Mapping for Ultrasonic Characterization of the Microstructure in Ti-6Al-4V.

TASK: 191

TASK TITLE: High Performance Polymers

TASK OBJECTIVE: To provide structural tailoring of high performance polymers for Air Force applications.

SCIENTIST: Dr. Narayanan Venkatasubramanian

DESCRIPTION OF WORK:

Aromatic benzobisazole rigid-chain polymers with sulfonic acid pendants, by virtue of their reactivity and newfound processability in organic solvents, are potential multifunctional materials in high performance application areas such as ionic conductors, fuel cells, coatings as well as structural polymers for compressive strength. This report describes in detail the synthesis and characterization of a new monomer, i.e., 2,5-disulfoterephtahlic acid and its utilization in polycondensation reactions to synthesize disulfo-PBT and disulfo-PBI, para-ordered rigid-rod polymers with two sulfonic acid pendants. The corresponding model compounds have also been synthesized by the reactions of 2,5-disulfoterephthalic acid with o-aminothiophenol or o-phenylenediamine in polyphosphoric acid. The strong acidity of the model compounds as well as the polymers was borne out by their solubilization as their ammonium or sodium salts in water and as their trialkylammonium salts in alcohol. A study of their thermal characteristics reveals a well-defined degradation pattern, involving a first-stage weight loss due to the sulfonic acid pendant and a second-stage weight loss due to the degradation of the aromatic benzobisazole structure. The higher thermal stability of the sulfonic acid pendant in the benzobisimidazole system is attributed to its partial sulfonate salt-like character arising from its protonation of the imine structure of the heterocycle.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 179, Rigid-chain PBX Polymers with Two Sulfonic Acid Pendants for Structural and Conducting Applications.

TASK: 192

TASK TITLE: Polymer Photovoltaic Devices and Materials

TASK OBJECTIVE: To quantify the photophysics and conduction mechanisms in conducting and electro-optical polymers using photovoltaic response and related methods. The parameters to be determined are energy gap, carrier sign,

carrier lifetime, mobility, shape of the absorption edge, and quasi-particle energy levels.

SCIENTIST: Dr. Barney E. Taylor

DESCRIPTION OF WORK:

The knowledge about the photoconductivity (PC) of 6FPBO-OD has been increased by several investigations: The effect of a continuous bleaching light on the observed PC data is extended. An alternate method of normalizing the PC data has been developed that yields photoconductivity per incident photon. Finally, the first purely photovoltaic measurements have been performed on 6FPBO-OD.

Previous work had shown the presence of a bleaching effect when a continuous light of proper energy is shone on a 6FPBO-OD sample during a PC experiment. The earlier report suggested that the onset of the bleaching might occur at energies significantly larger than the band edge of the material. A more thorough set of experiments indicates that the onset of bleaching occurs at the band edge of the absorption (or at the onset of PC).

Earlier work had normalized the raw PC data by a technique based on comparing the output of the PC system's monochromator to the spectrum of a calibrated lamp. Such normalization lead to reduced data that were believed to be spectrally correct but arbitrarily scaled. A new technique, based on a calibrated photodiode, has been used to perform a normalization that yields PC per photon. The two methods generated spectra of significantly different shape. However, the cause of the discrepancey is not yet understood.

The first measurements of the dc values of the open circuit voltage, short circuit current and the current-voltage curves for 6FPBO-OD devices have been measured under white light. An open circuit voltage of 0.76 V was observed. However, the short circuit current of 37 pA is disappointingly low - probably because of the high internal resistance of 6FPBO-OD. The I-V data shows diode behavior and also changes in the expected manner when the sample is illuminated during I-V measurements.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 159, Expanded Photovoltaic Studies of the Polymer 6FPBO-OD.

TASK: 193

TASK TITLE: Development of Coating Life Prediction Tools

TASK OBJECTIVE: The objective of this task is to develop life prediction tools for corrosion protection performance evaluation including accelerated test methodologies and screening tests for future aircraft coating systems.

SCIENTIST: Ms. Natalia Voevodina/Dr. Seva Balbyshev

DESCRIPTION OF WORK:

Developing high performance corrosion protection coatings for aerospace applications that will be effective for 30 plus years service presents a number of challenges. Advances are needed in resin materials, formulation methods, and corrosion protection schemes.

The techniques used to evaluate the performance of coatings also need improvement. Currently, testing relies heavily on salt fog exposure testing that takes a significant amount of time, yields only qualitative results, and does not correlate well with field experience. A rapid test method that gives quantitative and mechanistic information of coating performance is needed to screen materials and formulations in support of development efforts. The same method, or a companion, that predicts long term performance is needed qualification testing.

Electrochemical techniques hold promise to provide both mechanistic information as well as a rapid assessment of coating system performance. The test methods and results will be discussed.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 157, Development of Coating Life Prediction Tools.

TASK: 194

TASK TITLE: Microstructure Evolution During Equal Channel Angular Extrusion (ECAE)

TASK OBJECTIVE: To establish the effect of ECAE deformation on breakdown of titanium alloys with a colony alpha microstructure.

SCIENTIST: Dr. David P. Delo

DESCRIPTION OF WORK:

The ECAE process for deforming bulk materials by simple shear was further developed by scaling-up the process of deforming Ti-6Al-4V from channel cross-sections of 1 inch x 1 inch to channel cross-section of 2 inch x 2 inch. Initial experimental results from the larger die system were consistent with the results obtained from the smaller die systems. Finite element analysis was aimed at analyzing the effects of frictional conditions and details of the die geometry to gain further insights into the characteristics of the process and to improve results. Initial possible improvements were identified and appropriate experimental trials are planned. Analysis of the effects of ECAE processing on microstructure and crystallographic orientation in Ti-6Al-4V was initiated. Further analysis of the experimental findings continues.

The effects of microstructural evolution and the resulting effects on mechanical properties were evaluated using the results of interrupted hot isostatic pressing experiments performed on Ti-6Al-4V powder. The microstructure was found to evolve from an initially martensitic condition to a coarser lamellar morphology during high temperature exposure during consolidation and subsequent mechanical testing. The microstructural and property changes were found to have implications for powder consolidation model calibrations that rely on mechanical testing of partially dense and fully dense compacts.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 154, Metallurgy and Advanced Metallic

Materials: Equal Channel Angular Extrusion of Ti-6Al-4V and Modeling of Ti-6Al-4V Powder Consolidation.

TASK: 195

TASK TITLE: Synthesis of nonlinear optical materials

TASK OBJECTIVE: To synthesize and characterize new nonlinear optical materials from aqueous solutions and organic solvents.

SCIENTIST: Prof. Zewdu Gebeyehu

DESCRIPTION OF WORK:

With the objective of preparing metal complexes which could be of potential use as nonlinear optical (NLO) materials, many transition and main group metal salts were reacted with sodium terephthalate, potassium iso-propylxanthate and sodium diethyldithiocarbamate ligands as well as the mixture of the later two, to synthesize complexes which possess extended $\pi$-system, contain polarisable group and crystallize in noncentrosymmetric space group respectively. The compounds prepared were characterized by spectroscopic method and few by elemental analysis. The nonlinear optical properties of the products isolated were tested by Kurtz method. Only complexes formed from the reaction of $CdCI_2$ with terephthalate and xanthate/diethyldithiocarbarmate mixed ligands gave promising results as NLO materials. The rest of the metal complexes prepared, failed to show NLO activity.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 156, Synthesis and Characterization of Metal Complexes Based Upon Xanthate, Diethyldithiocarbamate and Bridging Terephthalate ions which may be useful, as Nonlinear Optical (NLO) Materials.

TASK: 196

TASK TITLE: Durable/Cleanable Coating Development

TASK OBJECTIVE: The Air Force requires development of advanced aircraft coatings which incorporate high durability components and cleanable, stain-resistant formulations. The objective of this task is to develop enabling durable/cleanable coatings for future aircraft coating systems so that results from this task can be incorporated into coating systems beyond 2000.

SCIENTIST: Mr. Joel Johnson

DESCRIPTION OF WORK:

The main focus of this project was to evaluate various commercially available extender pigments for their gloss reduction efficiency, experimental critical pigment volume concentration (CPVC), and sensitivity toward different resin systems. In addition, an "incompatible blend" resin system was investigated in which the surface morphology obtained by phase separation of two resins creates a reduction in gloss. The most efficient extender from those examined in this project at reducing gloss and maintaining a low pigment volume concentration (PVC) to CPVC ratio, $\Lambda$, was Lovel-HSF precipitated silica. An established polyester urethane system required a PVC of 12.4% to obtain proper gloss with a $\Lambda$ value of 0.877. A simple two pigment formulation was also investigated in which 11.2% Lovel-HSF and 12.3% R-960 TiO2 PVC was required to meet the gloss specification for a white coating. This extender pigment was also treated with an aminosilane coupling agent to covalently bond it with the polyisocyanate portion of the resin. However, the high reactivity of the amine groups flocculated the extender particles causing large agglomerates. Approximately a 50% reduction in gloss was observed with the optimal unpigmented incompatible resin system of 1:1:1 dry volume of Desmophen 670A-80: Lumiflon-200: Desmodur N-3390 resins. The shapes of the gloss profiles as a function of incompatibility are similar for both the 60° and 85° gloss measurements. As expected, the film thickness played a role in the gloss obtained with thin films showing a higher gloss than thicker films, most likely because there is more incompatible resin volume to separate out in thicker films thus creating either more abundant or larger inclusion defects. The shapes of these domains are spherical when there is only a small amount of incompatible resin present, however, as the ratio of incompatible resin volume approaches 1:1 the included domain shapes become more disordered, probably due to the competition between each resin to become the continuous phase. The most promising formulation developed from both a PVC and $\Lambda$ standpoint was obtained through pigmenting an incompatible

resin blend with the Lovel-HSF silica. Both the lowest gloss PVC (9.8%) and Λ value (0.649) were obtained.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 163, Durable/Cleanable Coating Development.

TASK: 197

TASK TITLE: Theory of Two Photon Absorption

TASK OBJECTIVE: The objective of this task is to advance new techniques for modeling the two photon absorption process and apply these techniques to advanced organic and related materials.

SCIENTIST: Dr. Guru P. Das

DESCRIPTION OF WORK:

For long incident pulses, one-photon absorption in the excited state formed following a two-photon absorption can play a very significant role in some organic materials. We develop here a quantitative model to determine the contribution of excited state absorption in the interpretation of the two-photon absorption data for such materials. We present representative calculations of this effect for some selected systems.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 164, A Theoretical Model For Excited State Absorption.

TASK: 198

TASK TITLE: Modeling and Simulation of Novel Conjugated Materials

TASK OBJECTIVE: The objective of this task is to predict molecular and polymeric properties important in the development of new conductive and semiconductive organic materials.

SCIENTIST: Dr. Xiaofeng Duan

DESCRIPTION OF WORK:

Density Functional Theory (DFT) was used to investigate the geometries and electronic structures for six aromatic-bis(squarate) model compounds and their dianions as well as their reduction products in four different configurations. The single point energies were calculated for all the reactants and products at the B3LYP/6-311+G(2d,p)// B3LYP/6-31G(d) level. In addition, the vibrational frequencies of all the species were calculated from which thermodynamic properties were evaluated. The integral equation formalism for the polarizable continuum model (IEFPCM) was employed to obtain the solvation energies for the model compounds and their dianions. The electrode potentials for the two electron reductions of the model compounds were studied and compared with experimental measurements.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 173, Reduction Processes of Aromatic-Bis(squarate)s.

TASK: 199

TASK TITLE: Synthesis and Characterization of Thiazole Materials

TASK OBJECTIVE: To synthesize monomers, oligomers and polymers of thiazole, bithiazole and related materials and to explore their derivitization for chemical reduction.

SCIENTIST: Dr. Mark D. McClain

DESCRIPTION OF WORK:

Polymers containing quaternized benzimidazole rings are predicted to form stable conducting polymers upon n-doping. Phenyl-, thienyl-, and pyridyl-bridged N-ethylated benzimidazoles were synthesized and computationally modeled by molecular orbital theory calculations.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 162, Synthesis and Characterization of Thiazole Materials.

TASK: 200

TASK TITLE: Computational Design of Low Friction Surfaces for Microelectromechanical Systems (MEMS)

TASK OBJECTIVE: To develop a structure-property-application based strategy for evaluating the thermal stability and frictional characteristics of model self-assembled monolayers (SAM) for MEMS applications. And to extend and refine computational methods to studying friction at an atomistic level.

SCIENTIST: Dr. Martin Schwartz

DESCRIPTION OF WORK:

Self-Adsorbed Monolayers (SAMs) of alkyltrichlorosilanes have proved potentially useful as lubricants for Microelectromagnetic Systems (MEMS). In order to test the effects of various substituents on alkylsilanes chemisorbed on silica surfaces, we have undertaken an ab initio quantum mechanical investigation of Si-O Bond Dissociation Energies (BDEs) on a serious of mono- di- and trisubstituted siloxanes and silanols, YH2SiOX, Y2HSiOX, Y3SiOX, Y=Me, F, Cl, OH, X=SiH3 (siloxanes), H (silanols). It was observed that fluorine and chlorine substituents induced a marked increase in the BDE of the proximal Si-O bonds (R3Si-OX). Somewhat surprisingly, these substituents also enhanced the distal Si-O bond strengths (R3SiO-X). Hydroxy substituents induced a large proximal BDE increase, but a much more modest increase in the bond strength of the distal Si-O bond. Methylation caused a small increase in the proximal BDE, and

had no impact on that of the distal bond. A comparison of the observed trends with parameters characterizing inductive electronic and spin delocalization effects, together with observed bond length trends, revealed that the above trends result from a combination of both ground state stabilization as well as destabilization of the radicals. From the results of this study, it is concluded that the stability of alkyl silane SAMS in MEMS devices can be improved by addition of fluorine, chlorine or hydroxy groups to the lubricant's silicon atom.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 211, Computational Design of Low Friction Surfaces for Microelectromechanical Systems (MEMS).

TASK: 201

TASK TITLE: Computational design of low dimensional conductive organic crystals for composite applications

TASK OBJECTIVE: The objective of this task is to employ molecular modeling techniques to optimize the molecular structure, crystal structure and growth habits or organic crystals to produce conductive molecular wires.

SCIENTIST: Dr. Douglas Miller

DESCRIPTION OF WORK:

An effort was initiated to study conductive crystals and charge-transfer complexes for use in coatings or conductive polymers. Bechgaard salts and other organic, charge-transfer complexes were studied. Computational work studied the morphology of Bechgaard salts. Synthetic effects produced a water-soluble electron donor for future experimentation.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 161, Computational design of low dimensional conductive organic crystals for composite applications.

TASK: 202

TASK TITLE: Metal Matrix Composites Support

TASK OBJECTIVE: Provide uniquely specialized support to the metal matrix composites activity.

SCIENTIST: Dr. Warren H. Hunt

DESCRIPTION OF WORK:

This report describes activities in support of the Air Force Research Laboratory, Materials and Manufacturing Directorate's metal matrix composite efforts. Specifically, the work involved assistance in identifying the opportunities and technical challenges for the use of particulate-reinforced metals in future aeronautical and space systems. This information, gathered through literature review, a workshop, and personal contacts, was summarized and provided for inclusion in a technical report in collaboration with Air Force Research Laboratory, Materials and Manufacturing Directorate personnel.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 209, Metal Matrix Composites Support.

TASK: 203

TASK TITLE: Development of Phase Field Approach to Microstructural Evolution of $\gamma'$ Precipitates with Simultaneous Nucleation, Growth and Coarsening

TASK OBJECTIVE: Provide uniquely specialized support to the metal matrix composites activity.

SCIENTIST: Dr. Yunzhi Wang

DESCRIPTION OF WORK:

This report summarizes the effort towards the development of a phase field model of microstructural evolution of γ' precipitates in nickel-base superalloys. Because of its abilities to treat high volume fractions of ordered intermetallics and coherent strain energy of transformations, the phase field model is ideal for modeling γ' precipitation in these alloys. At present, however, applications of the phase field model are limited to isothermal conditions with site saturation approximation for nucleation. Such conditions cannot generally be realized in practice because of competing constraints. This work extends the phase field model to simultaneous nucleation and growth processes by incorporating a stochastic model of nucleation, in which nuclei are added explicitly to the evolving microstructure according to the nucleation rate that could be supplied by either experiment or atomistic modeling. During the simulations the nucleation rate is dynamically adjusted as temperature and matrix composition vary. Several examples including both isothermal aging and step-quenching simulations are discussed. The model has been validated against the standard Johnson-Mehl-Avrami-Kolmogorov analysis. The semi-implicit spectra codes of the method are being optimized on the distributed environment at the Air Force Major Share Resource Center.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume

TASK: 204

TASK TITLE: Ni-Based Co-Continuous Ceramic Composite: Processing and Characterization

TASK OBJECTIVE: The objectives of this task are to further the development, understanding and potential application base for co-continuous ceramic composite (i.e., C4) materials; investigate the processing of these materials on a bulk scale; and assess the mechanical behavior, thermophysical properties and microstructure.

SCIENTIST: Dr. Michael C. Breslin

DESCRIPTION OF WORK:

Investigations into simplifying and expanding the robustness of a process for producing a unique, low cost, co-continuous ceramic composite (i.e., C4) material comprised of α-Al2O3 and any of a variety of alloys (e.g., Fe alloys, Ni alloys, Cu alloys, etc.) were conducted. A new rapid prototyping/manufacturing technology known as directed light fabrication (DLF) was evaluated for its compatibility with the C4 materials, as were refinements in the relevant reactive metal processing equipment. Although results definitively suggest that additional research is necessary, preliminary data indicate that not only is the DLF process compatible with the C4 technology, but the manufacture of these materials is amenable to foundry equipment rather than the specialized equipment currently being employed.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 206, Ni-Based Co-Continuous Ceramic Composite: Processing and Characterization.

TASK: 205

TASK TITLE: Advanced Compliant Universal Substrate Bonding Technology

TASK OBJECTIVE: To develop and test an in-house bonding facility for creating compliant universal substrates.

SCIENTIST: Dr. Trice Walter Haas

DESCRIPTION OF WORK:

Compliant universal substrate (CUS) technology offers great promise for the realization of multimaterial multifunction integrated circuits. A necessary step in achieving CUS is the need to bond together two wafers having appropriate epitaxial layers grown on them by molecular beam epitaxy or other similar techniques. This task concentrated on first the construction of an appropriate wafer bonding furnace and finally on a study of some interfacial chemical effects on the bonding process. A sophisticated wafer bonding facility was established and demonstrated that is very versatile and capable of bonding substrates up to three inches in diameter. Bonding

demonstrations were performed on GaAs wafers and the beneficial effects of a technique known as arsenic capping on interface chemistry of the bonded wafer were also demonstrated.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 177, Advanced Compliant Universal Substrate Bonding Technology.

TASK: 206

TASK TITLE: Capacitance Dispersion in Ion Implanted 4H and 6H-Silicon Carbide

TASK OBJECTIVE: Deep Levels in Bulk and Epitaxial Silicon Carbide

SCIENTIST: Dr. Andrew O. Evwaraye

DESCRIPTION OF WORK:

Nitrogen doped 4H-SiC and 6H-SiC epitaxial layers with net doping concentrations of 1.5 x $10^{15}$ $cm^{-3}$ were implanted with Al or B ions at 600° C. The energy of the ions was 160 keV and at a dose of 2 x $10^{16}cm^{-2}$. After annealing at 1600°C for 5-30 minutes, Schottky diodes were fabricated on the samples. The measured junction capacitance varies with both termperature and frequency. The thermal activation energy determined from the frequency break $\omega_B$ shows that the defect responsible for the observed dispersion is Al or B impurities. However, the junction capacitance of samples doped with Al does not exhibit dispersion. Therefore, while Al and B are shallow acceptors in silicon carbide, in the presence of N donors they behave like deep acceptors. The slow response of these "deep acceptors" to AC signal accounts for the observed dispersion. The data shows that the series resistance is insignificant and therefore does not account for the observed dispersion.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 200, Capacitance Dispersion in Ion Implanted 4H and 6H-Silicon Carbide.

TASK: 207

TASK TITLE: Shubnikov-de Haas Study of Gallium Nitride Based Heterostructures

TASK OBJECTIVE: The objective of this task is to measure effective masses and scattering times in gallium nitride based heterostructures such as AlGaN/GaN and AlGaN/InGaN/GaN and compare these with values for conventional III-V heterostructures.

SCIENTIST: Dr. Said Elhamri

DESCRIPTION OF WORK:

We have studied several AlxGa1-xN/GaN structures grown by different growers. Three methods of characterizations were used: The conventional Hall effect, the Shubnikov de Haas effect, and X-ray. Following is a report on a detailed study of one of these AlxGa1-xN/GaN structures whose aluminum mole fraction x = 0.13. The structure was deposited by molecular beam epitaxy on a GaN layer grown by organometallic vapor phase epitaxy on a sapphire substrate. At 10K, conventional Hall effect measurements produced a sheet density of 5.1x1012 cm-2 and a mobility of 1.9x104cm2/Vs. At low temperatures, mobility spectrum analysis confirmed the presence of a single carrier transport and revealed the presence of negligible parallel conduction. The shubnikov-de Haas studies produced carrier densities that were in good agreement with those from the Hall effect. The effective mass was found to be 0.215±0.006m0. The quantum ($\tau q$) and the transport ($\tau c$) lifetimes were also calculated. The ratio $\tau q/\tau c$ was about 5 where $\tau c = 2.3 \times 10^{-12}$s. X-ray diffraction studies revealed that the thin AlGaN layer was coherently strained to the thick GaN layer. Methods for computing the aluminum mole fration in the AlGaN layer by x-ray diffraction are also discussed.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 202, Shubnikov – de Haas study of gallium nitride based heterostructures.

TASK: 208

TASK TITLE: NDE Research on Optical Detection of Ultrasonic Waves

TASK OBJECTIVE: The objective is the development emphasizing high resolution, high speed measurement of phase jitter which will provide information on microstructural features of the material.

SCIENTIST: Dr. Peter B. Nagy

DESCRIPTION OF WORK:

A high resolution experimental capability has been developed to map the phase and magnitude of ultrasonic waves transmitted in a solid. The advancement presented in this report is provided by laser detection of the ultrasonic energy over a microscopic aperture of approximately 50 mm and a special high-sensitivity phase mapping configuration. The system is built around a computer controlled scanner and a confocal Fabry-Perot interferometer, which uses a diode pumped Nd:YAG laser as a light source. Wave propagation in the axial and radial directions of a 2.5"-diameter bar of highly textured Ti-6Al-4V was investigated in this study. The work was motivated by the observation of unusually high attenuation in the axial direction of the as-received bar, which was thought to be associated with phase distortion rather than intrinsic attenuation loss. The current phase mapping results, using a focused laser spot, show relatively high wavefront distortion and more nonuniform distribution of the transmitted energy in the axial direction. The contribution to attenuation associated with phase cancellation loss was also investigated. These measurements show the laser detected attenuation to be substantially lower than the piezoelectrically measured coherent attenuation. However, even the relatively phase-insensitive focused laser detection clearly indicates that the attenuation is stronger in the axial direction.

The special phase-mapping technique developed in this project was also adapted to high-speed ultrasonic phase jitter measurements in a cost-sharing effort with the Ohio Aerospace Institute. We successfully verified the feasibility of this technique for ultrasonic flow measurements that are capable of accurately assessing the mass flow rate in small-diameter fuel line tubes at very fast sampling rates without any interference with the fluid flow. This technique will help aircraft engine designers better understand the role of adverse fuel line feedback mechanisms in the

formation of destructive combustion instabilities called "acoustics" as well as other performance characteristics of liquid fuel atomizers, that directly affect combustion efficiency, pollutant emission, and flame stability.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 170, High Sensitivity Phase Measurements for Ultrasonic Data Evaluation.

TASK: 209

TASK TITLE: Second Layer Crack Detection in Aluminum Aircraft Structures

TASK OBJECTIVE: To investigate the potential of Remote Field eddy current inspection (RFES) to detect cracks in the second layer of aluminum bolted aircraft structures.

SCIENTIST: Dr. Yushi San

DESCRIPTION OF WORK:

The remote-field eddy-current system, RF-01, made by Innovative Materials Testing Technologies, Co. (IMTT), has been used to detect cracks in the specimens made by Look-Georgia Company. The specimens are built to simulate aircraft two-layer aluminum structures with fasteners. The total thickness for Specimen Group A is 0.256", for Group B is 0.446". Cracks are made on different layers and different surfaces. The test was done at WPAFB, OH and IMTT, Ames, IA. Improvements to the system and the probes have been made during the project time. The final results have shown high sensitivity of the RF-01 system to cracks of both specimen groups and at difference depths and feasibility of the system working with a scanner.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 166, Second Layer Crack Detection in Aluminum Aircraft Structures.

## Extended Tasks (11/3/99 – 12/15/99)

TASK: 173A

TASK TITLE: Threshold Crack Growth Behavior in Titanium Alloys

TASK OBJECTIVE: To evaluate the effects of crack geometry and crack length on the threshold and near-threshold crack growth behavior in titanium alloys under combined low cycle and high cycle fatigue. To develop mechanistic models for predicting the crack growth threshold in titanium alloys as a function of load history and stress state near the crack tip.

SCIENTIST: Dr. Weiju Ren

DESCRIPTION OF WORK:

Investigation under contract number F33615-94-C-5804 is continued on two of the major causes for high cycle fatigue problems in airplane gas turbines. The investigation is divided into two projects: 1) Interaction of low cycle fatigue and/or creep effects with subsequent high cycle fatigue, and 2) Fretting damage and coating effects on high cycle fatigue. Specimens have been machined for both projects and some of the fretting specimens have been prepared with the first kind of coating. Mechanical testing for fretting fatigue has been started. Microstructural characterization and finite element analysis preparations, literature review and DOD clearance check are underway. The investigation will provide information for some fundamental understanding of high cycle fatigue and related mechanisms for the National High Cycle Program of the U.S. Air Force.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 195, Threshold Crack Growth Behavior in Titanium Alloys.

TASK: 175A

TASK TITLE: Development of Antistatic Repair Coating

TASK OBJECTIVE: The objective of this task is to develop an advanced antistatic repair coatings that provide long-term conductivity and ease of repair for future aircraft coating systems.

SCIENTIST: Dr. Thomas Fabish

DESCRIPTION OF WORK:

The present work completes an extension of the first phase of ABDR development performed under the previous task. The extension encompasses scaling up the recommended hand application system to a volume that can support limited field tests by Maintainers and evaluating alternate processing methods to our sand mill procedure that are suited to making multi gallon quantities of ABDR. [The parenthetical use of 'traditional' refers to coating systems that utilize a high volume loading of conductive particulate to impart electronic conductance to the composite film.]

Three quarts of the recommended hand application ABDR formulation were made for limited field tests by Maintainers scheduled for early January 2000. Feedback from Maintainers is important to iterating the ABDR formulation to meet broadest demands. A variety of hand application tools were purchased for the tests. These include foam rollers and brushes, bristle brushes, metal and plastic draw down blades all from the local hardware supermarket.

A comparison was performed between this sand mill system and a closely comparable system processed by three roll mill. Tests on films made from both show the sand mill system differs substantially in key film properties from three roll mill. The sand mill batch gives properties consistent with previously reported values for surface conductance, color, gloss, and pencil hardness. Three roll mill gives a low conductance outside ABDR specifications. Color and gloss also differ significantly from sand mill. This result illustrates the general sensitivity of paint systems to processing. Further optimization of three roll dispersion of our ABDR formulation should bring properties into specification.

Large area damage patterns in a four layer stackup on glass fiber reinforced composite were repaired using the scaled system to provide panels suitable for RF transmission and reflectance measurements that might gauge the potential cost of ABDR to RCS. Further development of 'traditional' ABDR systems as well as evaluation of a new and innovative materials design strategy based on highly conductive organic crystalline salts will be pursued under a new task.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 198, Development of Antistatic Repair Coating.

TASK: 177A

TASK TITLE: Mechanical Behavior and Toughness of Fibrous Monolithic Ceramics

TASK OBJECTIVE: To develop an understanding of the complicated fracture behavior in highly textured ceramics.

SCIENTIST: Dr. James Staehler

DESCRIPTION OF WORK:

Fatigue tests were performed on plain weave melt-infiltrated C/SiC at 1200°C in air. Dog-bone shaped specimens were machined by the manufacturer from one of two plates and given a thin protective overcoat (CBS-coating, AlliedSignal Composites, Inc.) to increase oxidation resistance. During fatigue testing, peak stresses ranged from 75-175 MPa with frequencies of either 1, 10, or 100 Hz. Frequency was found to play little, if any, role in the life of the material. Oxidation damage and peak stress were the primary factors controlling time to failure. As expected, higher peak stresses resulted in shorter lives for any given frequency. In addition, specimens from one plate consistently out-performed those of the second. Oxidation damage was apparent in all fractured specimens and progressed in from the edges despite the protective overcoat. There was little evidence of oxidation damage progressing in along the direction normal to the plane of the composite.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 199, Frequency Effects on the Fatigue Life of Melt-Infiltrated C/SiC at 1200° in Air.

TASK: 178A

TASK TITLE: The Synthesis and Characterization of Water Soluble, Two-Photon Absorbing Chromophores for Non-Destructive Imaging Evaluation of Aircraft Paint

TASK OBJECTIVE: To functionalize the active two-photon absorbing dyes that were recently developed at AFRL/MLBP for water solubility.

SCIENTIST: Dr. Ram Kannan

DESCRIPTION OF WORK:

Efforts towards the synthesis of a fluorene derived, branched, two-photon absorbing dye are reported. The compound contains two fluorenyl benzothiazole units, linked to triphenylamine and is made to reveal the effect of branching on two-photon absorption.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 210, The Synthesis and Characterization of Water Soluble, Two-Photon Absorbing Chromophores for Non-Destructive Imaging Evaluation of Aircraft Paint.

TASK: 180A

TASK TITLE: Characterization, Imaging, Sensor, and Simulation Techniques of Thin Film Growth, Growth Processing, and Analysis

TASK OBJECTIVE: To continue to develop data collection and manipulation capabilities for implementation of characterization, imaging, sensor, and simulation techniques of thin film growth, growth processing, and analysis.

SCIENTIST: Mr. Donald Thomas

DESCRIPTION OF WORK:

This report describes a personal computer-based system to monitor insitu temperature of semiconductor materials using absorption band-edge spectroscopy (ABES).

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 186, A Personal Computer-Based Insitu Temperature Monitor Using Absorption Band-Edge Spectroscopy.

TASK: 181A

TASK TITLE: Molecular Modeling of Polysiloxanes and Silsequioxanes

TASK OBJECTIVE: The objective of this task is to study, using modern molecular modeling techniques, the behavior of (1) polysiloxanes having side-chain liquid crystalline character, and (2) silsequioxanes having various pendants and molecular architectures.

SCIENTIST: Dr. Rishikesh Bharadwaj

DESCRIPTION OF WORK:

Mesoscale modeling of the polymer intercalation and exfoliation process in layered structures have been initiated. The goal is to understand better the initial stages of the intercalation process. Polysilanes and polysilylenemethylenes have been investigated using atomistic molecular dynamics simulations to understand the structure-property relationships as a function of backbone flexibility. The work involves the prediction of the pressure-volume-temperature, diffusion and conformational aspects of these inorganic-organic polymers.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 201, Molecular Dynamics Simulation of Polymeric Materials.

TASK: 182A

TASK TITLE: Tribology of Quasicrystals

TASK OBJECTIVE: To characterize the friction and wear properties of quasicrystalline materials in different environments, and to characterize the chemistry and microstructure of quasicrystalline coatings and relate them to tribological properties.

SCIENTIST: Mr. Jeremy P. O'Neill

DESCRIPTION OF WORK:

Several AlCuFeCr coatings with various compositions were investigated for their surface energy. Although, Al2O3 does not have a low surface energy itself, coatings having increasing aluminum-containing-oxide had decreasing surface energy.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 194, Surface Energy of Coatings with Stoichiometries Close to the MC3 Approximant to Decagonal Quasicrystalline Phase in the AlCuFeCr System.

TASK: 183A

TASK TITLE: Plasma Deposition of Low Friction Hard Coatings

TASK OBJECTIVE: To develop new tribological films, which have novel microstructures, to enable multiple tribological functionality. To investigate the use of carbides, nitrides, and diamond-like carbon (DLC) in these films for load carrying and wear resistance and solid lubricant materials to provide low friction in dry, moist, and UHV environments. To understand the evolution of microstructure through the characterization of plasma energy.

SCIENTIST: Dr. Andrey Voevodin

DESCRIPTION OF WORK:

Interactions between plasmas produced by a nitrogen ion-beam source and pulsed laser ablation of Al2O3 were studied. Plasma emission imaging and spectroscopy analysis were applied to investigate plasma development and chemistry in real time using laser pulses for synchronization. Film elemental compositions were correlated with plasma chemistry. Two significant plasma interaction effects were discovered. One resulted in a considerable activation of N and O and formation of NO in a near substrate region, which then reacted with Al to from Al-O-N. Another interaction effect was observed in the 2-4 Pa pressure region, when formation of short lived plasma channels connecting ion-beam and laser ablated plasmas was detected. The study suggested that the interaction of ion-beam and laser ablation plumes in IAPLD might considerably affect plasma chemistry, excitation stages, and spatial distribution, providing new opportunities for the control of the oxide-based tribological films.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 196, Plasma Deposition of Low Friction Hard Coatings.

TASK: 185A

TASK TITLE: Surface Chemistry and Performance of Spacecraft Lubricants

TASK OBJECTIVE: To determine the nature of friction and wear of spacecraft materials from a surface chemistry and performance perspective.

SCIENTIST: Dr. Jeffrey N. Cutler

DESCRIPTION OF WORK:

New material systems hold promise for increased reliability, lower torque noise and longer lifetimes in high-speed bearings for spacecraft. These new materials include stable, low volatility fluids in conjunction with alternative solid surfaces: either new bulk materials or surface modifications effected by treatments or coatings. In order to study these materials in a simulated

space environment, a series of vacuum testers have been developed which allow performance testing in the 10-7 Pa regime. In particular, an eccentric bearing test has been developed to screen additives and lubricants within a starved lubrication regime.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 204, New High Speed Eccentric Bearing Test for Spacecraft Applications.

TASK: 187A

TASK TITLE: Heterointerface Formation during MBE Growth of Semiconductor Thin Films: Growth Modeling and Heterointerface Characterization

TASK OBJECTIVE: To develop and use computer models of MBE growth to determine the optimal growth conditions to obtain heterostructure materials with compositionally uniform layers and atomically flat interfaces.

SCIENTIST: Dr. Krishnamurthy Mahalingam

DESCRIPTION OF WORK:

Transmission electron microscopy (TEM) studies were performed on GaAs layers grown epitaxially on standard (511)-Si and compliant-Si substrates. Significant reduction in the density of threading dislocations (approximately three orders of magnitude) is observed in the GaAs layer grown on the compliant-Si substrate. A noise reduction procedure for digitized high-resolution TEM images has been implemented base on Wiener noise analysis.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 187, Transmission Electron Microscopy of Semiconductor Thin Films.

TASK: 188A

TASK TITLE: Processing and Characterization of High-Performance Polymeric Materials for Space and Rocket Applications

TASK OBJECTIVE: To provide a fundamental understanding of the structure/property relationships that exist for high-performance polymeric materials identified as leading candidates for use in rocket and space applications. The benefits from this study will be a more thorough understanding of the properties of specific thermoplastics which result from various modifications to the chemical structure of the materials and the ability thereby to tailor this class of materials for optimal performance.

SCIENTIST: Dr. Hong Guk Jeon

DESCRIPTION OF WORK:

In this work, the synthesis and characterization of a new series of wholly-aromatic copolyesters derived from the condensation of various weight fractions of 4,4'-(o-phenylenedioxy) dibenzoic acid (OPDB) and substituted terephthalic acid (BTA) with 2-phenylhydroquinone (PHQ) are discussed. The Higashi method, involving tosyl chloride and pyridine as solvent, was employed to yield polymer with significant molecular weight. These polymers are intended to enable accessible clearing transition and to control the balance of stiffness and toughness in melt-spun fibers systematically. The synthetic details along with characterization of quiescent phase behavior and morphology are reported.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 190, New Wholly-Aromatic Thermotropic Polyesters with Controlled Flexibility.

TASK: 191A

TASK TITLE: High Performance Polymers

TASK OBJECTIVE: To provide structural tailoring of high performance polymers for Air Force applications.

SCIENTIST: Dr. Narayanan Venkatasubramanian

DESCRIPTION OF WORK:

Aromatic benzobisazole rigid-chain polymers with sulfonic acid pendants, by virtue of their reactivity and newfound processability in organic solvents, are potential multifunctional materials in high performance application areas such as ionic conductors, fuel cells, coatings as well as structural polymers for compressive strength. This report describes in detail the synthesis and characterization of a new monomer, i.e., 2,5-disulfoterephthalic acid and its utilization in polycondensation reactions to synthesize disulfo-PBT and disulfo-PBI, para-ordered rigid-rod polymers with two sulfonic acid péndants. The corresponding model compounds have also been synthesized by the reactions of 2,5-disulfoterephthalic acid with o-aminothiophenol or o-phenylenediamine in polyphosphoric acid. The strong acidity of the model compounds as well as the polymers was borne out by their solubilization as their ammonium or sodium salts in water and as their trialkylammonium salts in alcohol. A study of their thermal characteristics reveals a well-defined degradation pattern, involving a first-stage weight loss due to the sulfonic acid pendant and a second-stage weight loss due to the degradation of the aromatic benzobisazole structure. The higher thermal stability of the sulfonic acid pendant in the benzobisimidazole system is attributed to its partial sulfonate salt-like character arising from its protonation of the imine structure of the heterocycle.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 192, Aromatic Benzobisazole polymers based on 1H-Pyrazole-3,5-diyl moiety.

TASK: 193B

TASK TITLE: Development of Coating Life Prediction Tools

TASK OBJECTIVE: The objective of this task is to develop life prediction tools for corrosion protection performance evaluation including accelerated test methodologies and screening tests for future aircraft coating systems.

SCIENTIST: Dr. Seva Balbyshev

DESCRIPTION OF WORK:

The main effort of this research was aimed at developing an environmentally benign replacement for chromate conversion coatings currently used in aircraft coating formulation. Series of silicon-only nanophased sol-gel systems were evaluated for corrosion protection properties by means of Electrochemical Impedance Spectroscopy. Several application procedures were investigated electrochemically: sol-gel applied to aluminum alloy and sol-gel applied to aluminum substrates previously coated with a thin layer of silicon coupling agent.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 191, Electrochemical Spectroscopy Analysis of Self-Assembled Nanophase Particle Coatings.

TASK: 197A

TASK TITLE: Theory of Two Photon Absorption

TASK OBJECTIVE: The objective of this task is to advance new techniques for modeling the two photon absorption process and apply these techniques to advanced organic and related materials.

SCIENTIST: Dr. Guru P Das

DESCRIPTION OF WORK:

The Mopac semi-empirical molecular code, which has already been modified to compute the two-photon absorption absolute cross section of chromophoes, is now capable of also estimating the excited state absorption contribution. Several two-photon absorbing systems are being studied in this semi-empirical framework in order to study theoretically the long-pulse limit on two-photon cross section.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 203, A Semi-Empirical Model for Excited State Absorption.

TASK: 198A

TASK TITLE: Modeling and Simulation of Novel Conjugated Materials

TASK OBJECTIVE: The objective of this task is to predict molecular and polymeric properties important in the development of new conductive and semiconductive organic materials.

SCIENTIST: Dr. Xiaofeng Duan

DESCRIPTION OF WORK:

During the period from November 3 to December 15, calculations on project of "Theoretical Investigation into the Reduction Potentials, Binding Energies and Nonlinear Optical Properties for the Poly(Benzobisthiazoles)" was continued and the writing-up of the project "Computer Prediction of Infrared Paint Signatures" has been finished.

The detailed project description, method, results, and discussion are reported in Contributive Research and Development Final Report, Volume 189, Quantum Mechanics Studies on Infrared Paint Signatures and Conducting Polymers.